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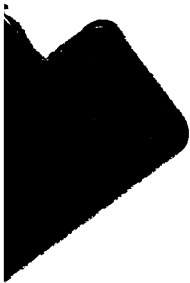
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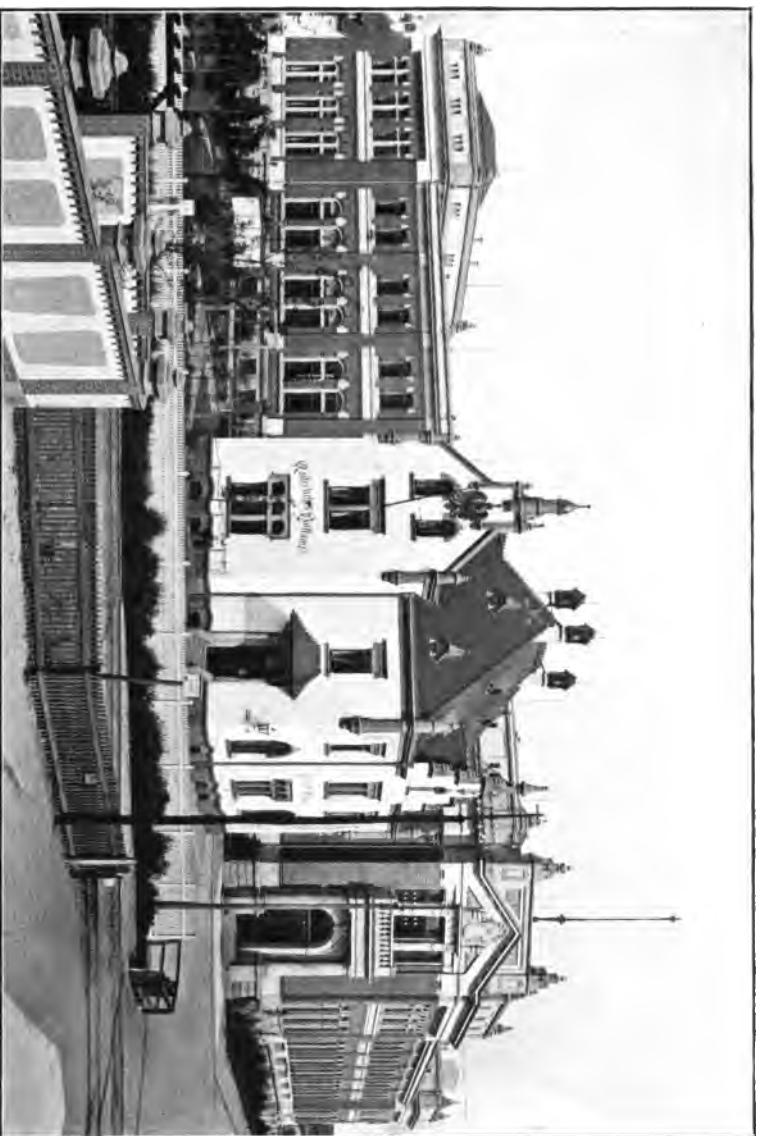
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Head Offices of Schimmel & Co. and Imperial Post and Telegraph Office at Miltitz.

SEMI-ANNUAL REPORT

W. B. Lawrence
SCHIMMEL & Co.

(MILITZSCHE BROTHERS)

MILITZ

NEAR LEIPZIG

LONDON • NEW YORK.



APRIL/MAY 1903.

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List of abbreviations.

d = specific gravity at 15° , unless otherwise stated.

$d_{20^{\circ}}$ = specific gravity at 20° .

$d \frac{20^{\circ}}{4}$ = specific gravity at 20° , compared with water at 4° .

$\alpha_{D_{15^{\circ}}}$ = optical rotation, at 15° , in a 100 mm tube.

$[\alpha]_D$ = specific rotation.

$n_{D_{15^{\circ}}}$ = index of refraction at 15° .

n = normal.

$\frac{n}{2} \left(\frac{n}{10} \right)$ = semi-normal or deci-normal (titrated solutions).

g = gramme; cc = cubic centimeter; mm = millimeter.

Temperatures are uniformly stated in centigrade degrees ($^{\circ}$).

Since the date of our last Report (October 1902) no decided change has come over the general economic situation in Germany. At the same time, it cannot be denied that in numerous branches of Industry features of a somewhat more favourable character are apparent, which manifest themselves in good dividends of the leading financial institutions and of a large number of important firms in other branches of Trade and Industry.

In spite of all competition and other difficult internal conditions, the Chemical Industry still continues its upward movement. Although at this moment it is not yet possible to bring forward statistic proofs in the form of comparative figures of the turnover and exports in support of this statement, we have yet valuable and reliable data in the statistics of the Manufacturers' Union of the Chemical Industry, according to which the number of chemical Works has increased in 1902 by 183, and that of the qualified workmen therein employed by 3487.

By way of comparison we give the figures of the last four years, as follows: —

	Number of works	Number of qualified workmen
1899	6589	135350
1900	6911	143119
1901	7169	153001
1902	7352	156488.

The foregoing figures show clearly that the German Chemical Industry has passed intact through the economic crisis of the last few years. Further, there are no grounds for fearing that it will be outstripped by competition from abroad, so long as the German Universities possess such eminent representatives of Chemical Science.

The Industry of essential oils and artificial perfumes has to place 1902 on record as one of its best commercial years. But yet it looks anxiously into the future, as the new German Tariff does not provide the relief which had been desired, and which is necessary for maintaining the trade in seed-oils.

In accordance with the Tariff now passed, the import duty on the so-called spice-seeds, such as anise, coriander, and fennel, has been raised from 3 to 4 marks per 100 kilos; on the other hand,

they may be admitted free under supervision on an official permit. But it is not stated whether what we at the time in our memorial had represented as absolutely necessary, has also received due consideration, viz., —

that the destruction of the seeds which have been distilled duty-free, as is usual with spices, under no circumstances can be considered practicable, as the residues are usefully employed as a valuable food for cattle; and that it is exactly this utilisation of the residues which renders the distillation at all possible, for in the competing countries, such as Holland, Russia, and Galicia, the profitable utilisation of the residue is a matter of very great advantage to the manufacturer of essential oils.

If this source of revenue is closed to the German manufacturer, his position will be even more unfavourable than hitherto, and the distillation of seed-oils will then become an impossibility.

As it can hardly be considered possible that agrarian influences have extended as far as this subject, we are really at a loss to understand why these just and carefully substantiated wishes for the prosperity and credit of the whole industrial branch, have not been taken into consideration, and we hope that it may yet be possible to grant the necessary concession by special decree.

The new Russian Tariff of January 13, 1903, has made unimportant changes as far as our industry is concerned. The import-duty on essential oils has remained the same (formerly 24 roubles + 10 per cent., now 26.40 roubles per pood); but on the other hand, the following increases, very disagreeable for the perfumery-trade, have been made: —

Aromatic waters without alcohol	from 4.77 to 7.95 roubles per pood.
Cosmetics, hair-dyes, etc., without alcohol	„ 13.60 „ 24,— „ „ „
Perfumes and cosmetics of every description, containing alcohol, such as perfumes, aromatic waters, elixirs, etc.	„ 29.75 „ 52.50 „ „ „

The import-duty on toilet-soaps, however, has remained unchanged. Nitrobenzene has been raised from 1.40 to 4.0 roubles per pood. Chemico-pharmaceutic preparations, previously paying 1.50 roubles, are now charged 5 roubles per pood.

It is to be hoped that the negotiations now about to be commenced between the two Governments, may lead to advantageous treaties on the “most-favoured nation” basis.

The project of the new Austrian Customs-Tariff also shows but unimportant alterations in the rates applying to our goods; and as far as this market is concerned, it may be confidently expected that the treaties will bring no changes of any consequence.

The situation in the Transatlantic export-markets is unfavourable, especially in Central and South America. Above all, the fluctuations in the exchange in Mexico and Brazil have a restraining effect on the purchasing power and credit of those countries.

On the other hand, the settled economic conditions in the United States of North America, still undergoing an enormous development, operate beneficially; the situation there has consolidated to such an extent, that even the Presidential Election of next year may have no influence on it.

The Chemical Industry will take only a very unimportant part in the Universal Exhibition to be held at St. Louis in 1904, as the last Exhibitions at Chicago and Paris have followed each other so rapidly, that there is a lack of novelties. Moreover, chemical products do not form suitable material for exhibition-purposes, a fact to which we have frequently called attention.

Our export trade to Japan, the Dutch Indies, the Philippines and Australia has been animated.

In Europe the state of the trade has been normal, and does not call for any remarks.

In order to extend our commercial relations with the Capital of the Empire, Berlin, and to offer our clients all the advantages of a modern installation, we have on April 1st opened a branch-office at the Spittelmarkt No. 4—7.

The same is the case with Hamburg, where our office is for the present at Neuburg 6.

We have included in the programme of our operations the manufacture of artificial mustard oil.

As an Appendix to the present Report, we publish for the first time a work on a new subject, entitled:

“Contributions to the knowledge of the pharmacological and physiologico-chemical behaviour of some volatile substances”.

This work, executed in the Institute for Pharmacology and Physiological Chemistry at Rostock i. M. under the direction of Professor Dr. R. Kobert, will be continued. We believe that we are justified in our supposition that it will meet with a considerable amount of interest.

In the half-year under review, the numerous and important movements in the values of several leading articles have brought about a

very animated business. The mild winter in Central Europe has prematurely promoted the vegetation of many plants used as raw material in our industry, and has increased the danger of ultimate injury by subsequent frosts. It is to be hoped that these fears will not be realised.

Almond Oil, pressed from apricot-kernels. On this subject it is reported from Marseilles, that the upward movement in Syrian apricot-kernels has communicated itself to all other sources of supply. It is said that in the whole of Syria at most 200 to 300 bales are still to be found. The prices have advanced in consequence from 68 to 76 francs, and they would be still higher, if the Californian kernels had not placed a check upon the rise. We have not yet followed the advance with our prices of essential and fatty oils, as we are for the greater part covered by contracts at low rates, but in a few months' time we may also be compelled to raise our quotations.

Almond Oil, Germ. Pharm. IV, pressed from sweet almonds. The high prices of Bari and Sicilian almonds continue to rule, and no change must be expected before next autumn. In Puglia the 1902 harvest has given a yield of only 40 000 to 50 000 bales instead of the 100 000 bales anticipated, and they have all been bought up by speculators. The same is the case with the last Sicilian harvest. As other cheaper qualities do not come under consideration for the manufacture of oil, these figures will have to be taken into account until the advent of autumn.

Oil of Amber. Oil of amber does not, strictly speaking, belong to the essential oils, as it is obtained as a by-product in the dry distillation of amber for the production of succinic acid, and therefore owes its origin to a pyrogenic reaction. The rectified oil, *Ol. succini rectificatum* of some Pharmacopœias, was formerly, and is probably still used medicinally on a small scale, chiefly maybe as a remedy against toothache, an addition to liniments, etc. It appears that this oil is much esteemed in England, as the demand for it from that country is fairly brisk.

As we obtain the crude oil of amber direct from the producer, and rectify it ourselves, we are in a position to give an absolute guarantee of the purity of our distillate; but it is not quite easy to obtain the rectified oil of the brightest possible colour, and special measures have to be taken to produce even a distillate of only a bright-yellow colour. Very little is known of the physical constants of rectified oil of amber, and for this reason we give below a short

table of the properties of some oils rectified by ourselves. This table shows that the product supplied by us is always of identic constitution.

$d_{15^{\circ}}$	α_D	$n_{D20^{\circ}}$	Acid Number	Ester Number
0,9281	+ 22° 32'	1,50820	6,5	8,95
0,9259	+ 24° 28'	1,50802	5,1	6,8
0,9277	+ 24° 36'	1,50957	5,78	3,85
0,926	+ 24° 40'	1,50857	5,09	4,37
0,9295	+ 26°	1,51083	5,5	5,0

All these oils were soluble in 4 to 4,5 volumes of 95 per cent. alcohol.

For this reason we were all the more surprised, when recently several consignments sent to England formed the subject of complaints. The samples of oils sent to us for comparison, to which the oil we were to supply should correspond, differed in such a pronounced manner from our distillates, that we could not help looking upon them with great suspicion. For four samples which had a much brighter colour than our rectified oil, we obtained the following values: —

$d_{15^{\circ}}$	α_D	$n_{D20^{\circ}}$	Acid Number	Ester Number
0,8835	+ 3° 4'	1,48863	—	4,9
0,8437	— 1° 53'	1,46367	5,4	3,3
0,873	+ 3° 14'	1,48122	12,7	6,0
0,8941	+ 12° 55'	1,48633	2,1	2,7

All these samples were more readily soluble in 95 per cent. alcohol than the oils mentioned before. An addition of alcohol could not, however, be detected.

The essentially lower specific gravity, the lower rotatory power, and the change in the index of refraction, pointed to the fact that all these oils contained larger proportions of lower boiling constituents than our distillate. A detailed examination, with which we are at this moment still occupied, will prove whether these oils may be claimed to represent pure oils of amber, or whether they have undergone some "improvement" by the addition of other resin-distillates.

Oil of Ambrette-seeds. The well-known natural phenomena in Martinique have been used as a pretext for a rise in the price of ambrette-seeds. The holders of stocks, however, did not meet with any reciprocal feeling on the part of the consumers, and were soon compelled to drop their tactics.

Material is now available in greater abundance than ever.

We were the first to produce oil of ambrette-seeds, and to place it on the market. It has now secured a firm footing in the high-class perfumery-trade. The liquid oil of ambrette-seeds which we added to our lists in October last year, also finds great favour; from

this oil the solid odourless constituents, which in the manufacture of the ordinary distillate pass over along with the latter, have been removed. For use in soap-perfumes, where a little more substance is desired, the concrete oil might perhaps be preferred for practical reasons, but for all other purposes the new liquid product is recommended. The high quotation of the latter is not by any means a fancy price, but fully agrees with the intrinsic value and the richness of this preparation.

Angelica Oil. Our own cultivation of angelica-plants, extending over about 12 acres in the immediate vicinity of our factory, has yielded last year such a rich crop of roots as never before. For this reason we have, after many years' scarcity, once more an abundant stock of angelica oil at low prices.

The method of distillation at our Works is most rational, as only such quantities of roots are gathered from day to day as can be submitted to distillation. By these means it is possible to prevent heating which in working up fresh roots causes so much trouble, and to produce an oil of unparalleled quality.

Anise Oil. It is at the present moment too early to state with certainty, how on the whole the sale of Russian oil has been, and what stocks of this oil are still in existence, but a certain firmness of the market is unmistakable. The forced sales of large parcels of crude oil, which took place in the previous year, have now only occurred on a moderate scale, and the prices would already be decidedly higher, if it had not been for the fairly considerable quantities of oil of 1901 which have been carried forward into the new season. The value of this article will chiefly depend on the weather-conditions prevailing during the next few months, but it appears to us that a decline of any consequence is out of the question, if only for this reason, that the present quotations are below the normal average value.

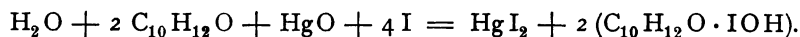
The export of anise from Libau, the principal anise-shipping port of Russia, amounted

in 1900 to	27518	poods,	of which	7744	poods	to	Germany
„ 1901 „	18659	„	„	„	6004	„	„

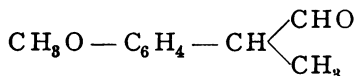
but it is possible that more important quantities than the above have found their way direct by rail from the anise-districts into Germany. The anethol-manufacturers had no lack of raw material. The Roumelian anise, already mentioned in our last Report, may possibly acquire some importance in the next few years. This anise yields a product of the highest quality, and should be preferred to the Russian seed on account of its purity.

New oxidation-products of anethol and analogous bodies with propenyl side-chain are discussed in Joseph Bougault's thesis¹⁾. If to a 1 per cent. solution of anethol in 96 per cent. alcohol, an excess of mercuric chloride is added, and then gradually a solution of about 1 per cent. iodine, the latter is immediately completely absorbed until 2 atoms iodine have been used up with one molecule anethol. The first superfluous drop then imparts a yellow colour to the liquid. On this Bougault bases a method for the determination of anethol and similar bodies with propenyl side-chain. But it can only be employed in the absence of bodies with double linkage, phenol- or amine-character, as these also react with iodine²⁾. The determination is carried out as follows: To the alcoholic solution of anethol, diluted to about 1 to 2 per cent., there is added 10 cc of an alcoholic solution of mercuric chloride (containing 6 per cent.), after which a titrated iodine solution is added drop by drop until the liquid is permanently coloured yellow. 254 g iodine correspond to 148 g anethol.

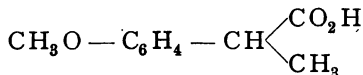
The reaction³⁾ which occurs in this process, is as follows: iodine and mercuric chloride form in the first instance iodine chloride, which, under the influence of the water of the alcohol, next splits up into hydrochloric acid and hypoiodous acid. The latter then attaches itself to the double linkage of anethol. This view is supported by the fact, that the same products are also formed when mercuric oxide and iodine are employed:



An excess of mercuric oxide produces a body which shows all the properties of an aldehyde, and which possesses the formula $\text{C}_{10}\text{H}_{12}\text{O}_2$. The same body is also formed, when the addition-product obtained with mercuric chloride is submitted to further treatment with mercuric oxide. The constitution of this aldehyde is expressed by the following formula:



for, when oxidised with silver oxide, it passes over into p-methoxy-hydratropic acid

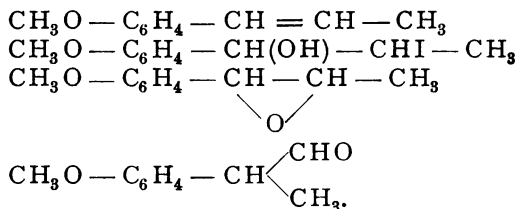


¹⁾ Thèse pour obtenir le grade de docteur, Paris 1902.

²⁾ Wijs, Zeitschrift für angew. Chemie 1898, 291.

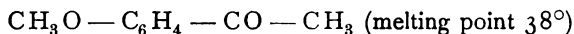
³⁾ For this reason the method is not applicable in practice to the determination of anethol contained in essential oils, as it only occurs in combination with bodies possessing double linkages, such as terpenes, methyl chavicol.

of the melting point 57° , and should therefore be designated as p-methoxyhydratropic aldehyde. Its formation is thus explained by Bougault:

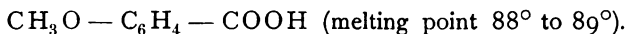


It forms a colour- and odourless liquid with a nauseous, burning taste, boils at 255° to 256° , and has the specific gravity at 15° of 1,069. Its bisulphite compound can be crystallised from water. The oxime obtained in the usual manner melts at 96° .

The acid belonging to it, or better still the bisulphite double-compound of the aldehyde, can by further oxidation be converted into the ketone



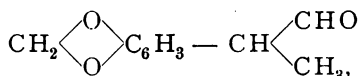
and the acid



Entirely analogous to anethol is the behaviour during these various reactions of isosafrol, methyl isoeugenol, and isoapiol. The bodies with allyl side-chain (such as methyl chavicol, safrol) also react in the same manner with iodine and mercuric chloride or mercuric oxide, but here the reaction is less pronounced, and an excess of mercuric oxide does not produce the corresponding aldehyde. A further difference between the two classes of bodies is this, that the addition-products from bodies with propenyl side-chain, when treated with silver nitrate, produce iodide of silver, and the aldehyde belonging to it, whilst those from bodies with allyl side-chain form iodide of silver but no aldehyde. On the other hand, the addition-products from all the bodies referred to, are reconverted into the crude material by zinc and glacial acetic acid.

The author has produced the following bodies by precisely the same methods as in the case of anethol:

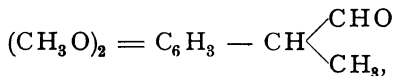
1. From isosafrol, methylene-3,4-dioxyhydratropic aldehyde



a liquid free from colour and odour. Boiling point 279° to 280° ; $d_{15} = 1,203$. Melting point of the oxime 71° . Melting point of

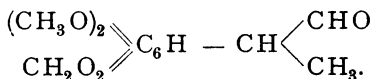
methylene-3,4-dioxyhydratropic acid 80° , and of methylene-3,4-dioxyacetophenone obtained from this acid 87° to 88° .

2. From methyl isoeugenol, dimethoxy-3,4-hydratropic aldehyde



a solid body of the melting point 44° . Melting point of the oxime 77° . The acid belonging to it, dimethoxy-3,4-hydratropic acid, melts at 60° , and the dimethoxyacetophenone formed from it, at 48° .

3. From isoapiol, dimethoxymethylene dioxyhydratropic aldehyde



This is a colourless liquid, boiling at 305° , and having a specific gravity at 15° of 1,246. It is almost insoluble in petroleum ether. The acid belonging to it, dimethoxymethylene dioxyhydratropic acid, melts at 97° , and the dimethoxymethylene dioxyacetophenone produced from it, at 92° .

Basil Oil. The freshly-distilled essential oil from *Ocimum Basilicum* L. (*Selasih hidjau*) rotates the plane of polarised light $0,35^{\circ}$ to the right, according to the observation made at the agriculturo-chemical laboratory of the Botanic Garden of Buitenzorg¹). If the oil is decomposed into fractions by steam distillation, and if the 10 per cent. first passing over are collected separately, this portion shows a dextrorotation of $+5^{\circ}$, whilst the residue rotates $0,6^{\circ}$ to the left. This residue, when heated, shows a remarkable optical behaviour. If, namely, it is heated up to nearly its boiling point, which lies at about 215° , and it is then cooled down, it is found that the previously slightly lævorotatory residue has become dextrorotatory ($+2^{\circ}$ in a 200 mm tube). But if it is heated for a prolonged time to a high temperature, the dextrorotatory power increases to $+3,4^{\circ}$, and appears to remain there permanently. On the other hand, by distillation in vacuo, only a body with a considerably lower dextrorotatory power can be isolated from the residue.

This peculiar optical behaviour of basil oil will be submitted to further examination.

Bay Oil. We have lately received such important consignments of genuine bay-leaves, that we were again able to supply exclusively our own distillate of the highest possible quality.

In addition to the 6 low-grade oils mentioned in our last Report, another large parcel of about 2300 lbs. imported in London from

¹) Annual Report 1901, 58.

Guadeloupe, has meanwhile also been placed on the market. The quality of this oil also shows abnormal properties. Whilst the content of phenols (eugenol and chavicol) of normal distillates fluctuates between 59 and 65 per cent., two samples of this Guadeloupe oil contained only 38 and 41 per cent. phenols. The specific gravity of the one was 0,934, that of the other 0,926; the optical rotation was $-2^{\circ}46'$ and $3^{\circ}10'$; against this, our own distillate has a specific gravity of 0,980 and a rotatory power of $-1^{\circ}48'$. We do not believe that the two samples mentioned above were adulterated, but attribute the differences to an irrational method of distillation.

In place of the so-called extra-strong bay oil which we previously kept in stock, we now supply an absolutely terpeneless quality, which in respect of its solubility answers still higher requirements than the former.

Cajeput Oil. According to reports from Macassar, the distillation in the Moluccas has suffered through severe drought. In various districts the plants have been completely destroyed, and only a limited quantity of oil has been distilled. Similar conditions have prevailed in the Straits Settlements, and as a consequence the values have risen considerably both in Singapore and in Macassar. As soon as the stocks in Holland, amounting at the close of the year to about 2000 bottles, have to some extent become depleted, a general increase in the prices, of about 30 per cent., will also be bound to take place in Europe.

Calamus Oil. We have already on a previous occasion¹⁾ referred to the results, recently published jointly by Thoms and Beckstroem²⁾, of their work on calamus oil. From these it appeared that asarone, which in the proportion of about 7,5 per cent. forms a constituent of this oil, has a genetic relation to the aromatic body of the oil. The asarone-content also explains the high methyl number, to which Benedikt and Grüssner³⁾ had already called attention. For, apart from minute quantities of eugenol and asarylic aldehyde, calamus oil does not contain any compounds with methoxyl-groups. Beckstroem⁴⁾ therefore proposes to make use of the asarone-content, in addition to the physical constants, in estimating the value of calamus oil.

Camphor Oil. Nothing new can be said of this article. We hear from Japan that the Camphor Monopoly Bill will again be laid before Parliament in the new Session, in May of this year.

A matter of exceptional interest was the report that a limited Company has been formed in New York under the style of "The Port

¹⁾ Report October 1902, 15.

²⁾ Berliner Berichte 35 (1902), 3187 and 3195.

³⁾ Chemiker-Zeitung 13 (1889), 1088.

⁴⁾ Berichte d. deutsch. pharm. Ges. 12 (1902), 266.

Chester Chemical Company", which has for its object the production of camphor by synthetic process. The share-capital amounts to 1 000 000 dollars, in 10 000 shares of 100 dollars each. According to the prospectus which we have before us, the world's consumption of camphor is said to amount to 8 000 000 lbs., that of the United States to 2 000 000 lbs.

It is claimed that the camphor produced synthetically is decidedly purer than the natural article (probably crude camphor) as it is received from Japan, or Formosa, for the purity of the latter is given as 88—90 per cent., that of artificial camphor as 99 per cent. The process is protected by patents.

The factory has been established in Fox Island, with plant for an annual output of 2 000 000 lbs. The immediate production is said to amount to 600 000 lbs.

The crude material employed is oil of turpentine, and the yield is 98 lbs. camphor from 1 barrel of the oil.

With the proposed maximum output of 2 000 000 lbs., the company expect to pay dividends of 50 per cent.

It appears to us that in the calculation the cost of turpentine oil of 6 $\frac{1}{2}$ cents per lb. is taken too low, in view of the present market-quotations, whilst the selling-price of camphor at 50 cents per lb. is taken a little too high. The Company may perhaps prosper, so long as the price of crude camphor in Japan is not reduced to such an extent that the estimates are upset. This new competition would probably only affect the value of the article, when the production exceeds the demand in the United States, and when the Company would be forced to export its product.

The prospectus of the Company contains the following interesting communications on the camphor production in Asia, taken from the reports of the American Consul in Formosa:

"Hitherto camphor has been produced from the wood of the camphor-tree which grows in Japan, China, and chiefly on the island Formosa. The production of Japan has fallen to 300 000 lbs., that of China has never exceeded 220 000 lbs., whilst that of Formosa in 1895 reached a total of 7 000 000 lbs., and in the last four years amounted on the average to about 6 000 000 lbs. For all practical purposes, Formosa therefore covers the world's requirements, and its production yields an annual revenue of about \$ 800 000 to the Japanese Government. In order to protect the industry, it is now obligatory to plant immediately a new tree for every camphor-tree which is cut down. The production in Formosa is moreover a monopoly, and is protected by 1500 armed guards who also control the afforestation as prescribed by law."

Cananga Oil. The stocks available in Holland and at Antwerp are only very insignificant, and consist partly of old stocks of inferior, viscid quality which gives a considerable loss in rectification, and which compares unfavourably in net cost with the fresh article imported

direct. Of the latter we have recently received important consignments, which enable us to offer an exquisitely fine, rectified, water-white oil at a very moderate price. The present quotation is certainly worthy of notice, for, according to reports from Java, at the present low values the manufacture is only carried on on a small scale, and it is expected that this diminished production will very soon find expression in the quotations.

Caraway Oil. The prices of Dutch caraway-seed have undergone but unimportant fluctuations in the course of the last six months. Several attempts made to drive up the values have been unsuccessful, and it would appear that the stocks are still too large to carry through, in the face of the new harvest, an increase in the quotations with any lasting result.

According to reports which have come to hand, the quantity sown this year would be approximately the same as that of 1902; for this reason, an upward movement would only be justified if the result of the harvest were injuriously affected by unfavourable weather-conditions.

From Sweden and Norway a few isolated small parcels were offered at disproportionately high prices. East Prussia and Finland supplied only insignificant quantities; on the other hand, several truck-loads of German caraway-seed were placed on the market, and were rapidly taken up by the consumers.

The prices of carvol, caraway oil, and carvene are at present well worthy of consideration.

Cassia Oil. The fluctuations of the last six months moved between the narrow limits of 1 d. to 2 d. per lb., according to the exchange of silver. Latterly, the high-grade oil containing 80 to 85 per cent. aldehyde, which is the one most in demand, has been somewhat more plentiful. The qualities which have lately come under our notice have not called for any remark, and it may therefore be assumed that the adulterators have given up their nefarious trade. But all the same, it will be well, in view of the Chinese character, to continue checking the quality by means of the determination of aldehyde.

Business in cassia oil has been remarkably slow. This is also confirmed by the figures of the Hongkong export. These figures, which comprise oils of cassia and of star-anise, were as follows: —

			in the year 1902 only	3635	cases
against	"	"	1901	6423	"
	"	"	1900	4261	"
	"	"	1899	3374	"
	"	"	1898	4461	"

Of the quantity of 1902, the shipments to America consisted of 1308 cases, against 2090 cases in 1901.

The last Chinese quotations, at the end of February, were: —
 for 70 to 75 per cent. oil \$195,— per picul = $2/8$ per lb. d/d Hamburg
 „ 75 „ 80 „ „ „ \$205,— „ „ = $2/9$ „ „ „ „
 „ 80 „ 85 „ „ „ \$215,— „ „ = $2/10^{8/4}$ „ „ „ „

The stock at Hongkong amounted to about 300 cases.

At the present prices we consider this article a good subject for speculation.

Cassia Oil “Schimmel & Co.” Although pure cinnamic aldehyde, free from chlorine, cannot at the present quotations compete with Chinese cassia oil, there are a fair number of consumers who use the first-named excellent product regularly for special purposes.

Pure cinnamic aldehyde has also been used of late to cover the disagreeable odour of many technical and pharmaceutical products. This applies in the first instance to benzene and ether (collodion). It should also be employed largely in all cases where hitherto cassia oil has been used as a spice, i. e. more particularly in the manufacture of the better-class confectionery, cakes, biscuits, condiments for cakes, and such like. In all these articles it is a question of the pure cinnamon-cassia flavour, and this is embodied in the pure aldehyde as in no essential oil. The manufacture, unfortunately, is not remunerative so long as the high-grade qualities of Chinese cassia oil are so low-priced, for the quotations of these two products must to a certain extent be proportionate to each other.

Oil of Cassie flowers. As mentioned by us on a previous occasion¹⁾, we succeeded at the time in isolating from the oil of cassie flowers (*Acacia Farnesiana* Willd.), in addition to methyl ester of salicylic acid and a ketone of a very pleasant violet-like odour, also benzyl alcohol, by means of phthalic anhydride. Recent examinations have shown that in all probability linalol and geraniol are also present. Further, we were lately able to obtain a crystalline compound, by shaking with bisulphite solution a fraction of the oil boiling from 95° to 105° at 11 mm. When this compound was boiled with soda solution, an aldehyde was soon split off, which was immediately identified by its intense characteristic odour as decylic aldehyde.

In a solution of glacial acetic acid it readily formed with sodium acetate and semicarbazide hydrochloride, a semicarbazone melting at 97° . By recrystallisation from benzene and petroleum ether, the melting point of the compound could not be raised to any appreciable extent,

¹⁾ Report April 1901, 18.

as the quantity of this aldehyde obtained up to the present was still very small. But in any case the aldehyde is identic with decylic aldehyde, whose semicarbazone melts at 102° . We obtained another aldehyde from a fraction boiling at 11 mm between 100° and 112° . This yielded with semicarbazide a solid semicarbazone, which, after repeated recrystallisation from alcohol, melted at 200° to 201° , and which was found to be the semicarbazone of cumic aldehyde. When this was heated with dilute sulphuric acid, an aldehyde was regenerated, which does not differ in its odour from cumic aldehyde. The melting point of the semicarbazone of the cumic aldehyde isolated from oil of cumin also lies at 200° .

At this moment we are still engaged on the further examination of the essential oils of *Acacia Farnesiana*, and of *Cassie Romaine*, and it is our intention, after a sufficiently thorough study, to report on this subject in detail.

A German Patent (No. 139635) has been granted to us for the use of the newly discovered bodies in the production of artificial oil of cassie flowers.

Cedarwood Oil, Atlas (Libanol Boisse). An exceptionally lively interest has been shown for this novelty, and at various clinical institutions examinations are now in progress on the therapeutical value of this product. If they confirm the favourable results obtained in the French hospitals, the use of this oil may become very extensive.

More recent information of a practical character has not been received from France.

Emilien Grimal¹⁾ reports in two communications the results of an examination made by him in our laboratory, of the essential oil of the Atlas cedar, *Cedrus atlantica*, a variety of *Cedrus Libani*. The oil examined had a peculiar odour, which is chiefly due to a ketone $C_9H_{14}O$ detected in the oil. The physical constants of the oil were as follows: $d = 0,9508$; $n_{D20} = 1,51191$; $[\alpha]_{D20} = +60^{\circ}32'$. The oil dissolved in 8,5 parts of 90 per cent. alcohol, and only in 115 parts of 70 per cent. alcohol. Acid number 1,16; saponification number 6,92; saponification number after acetylation 33,84.

In distilling the oil, 80 per cent. passed over between 270° and 295° . 800 g of the oil were fractionated; in the portions first passing over, small quantities of acetone were detected, and about 40 g were obtained of a fraction boiling between 180° and 215° , which contains the ketone $C_9H_{14}O$. This ketone yielded a semicarbazone of the

¹⁾ Compt. rend. **135** (1902), 582 and 1057.

melting point 159° to 160° , and an oxime which could not be obtained in the solid form, but which on brominating yielded a dibromide melting at 132° to 133° .

From the higher-boiling portions of the oil there was further obtained, as principal constituent, d-cadinene of the following constants: boiling point 273° to 275° ; $d = 0,9224$; $n_{D20^{\circ}} = 1,5107$; $[\alpha]_{D20^{\circ}} = +48^{\circ}7'$.

The hydrochloride produced from the latter showed the melting point 117° to 118° , and differs from the one hitherto known only by the opposite rotatory power, $[\alpha]_{D20^{\circ}} = +25^{\circ}40'$.

The cadinene regenerated from the dextrogyrate hydrochloride by Wallach's method, by means of sodium acetate in glacial acetic acid, showed the following constants: boiling point 274° to 275° ; $d = 0,9212$; $n_{D20^{\circ}} = 1,5094$; $[\alpha]_{D20^{\circ}} = +47^{\circ}55'$.

The hydrobromide melted at 124° to 125° .

The sesquiterpene also differs from the cadinene only by the optical rotation. A pure dextrogyrate cadinene had not hitherto been known.

Cedarwood Oil, Florida. It was recently found possible to reduce selling prices, as the offers of genuine cedarwood-chips were larger than before, and the manufacturers of lead-pencils were voluntarily making concessions. The distillation-expenses in our new factory are also essentially lower.

Celery Oil, from the fresh herb. The stock of this beautiful preparation has been completely cleared. We doubt very much whether the manufacture of this oil will again be taken up by us, as the number of consumers who are able to appreciate it is limited. This oil is one of those — like, for example, the garlic oil we used to manufacture — which are only appreciated when they are no longer obtainable.

Cinnamon Oil, Ceylon. The prices of fine cinnamon-chips have undergone fairly large fluctuations, until at last the downward tendency gained the upperhand. As a consequence, cinnamon oil could be produced under favourable conditions, and could be offered at such low prices as hardly ever before.

Citronella Oil, Ceylon. The prices of this important article reached their lowest position in October last year at about $8\frac{1}{2}$ d. per lb. The distillation was then completely suspended on account of continuous rainfall in the citronella-districts, and this led to a rise in the prices up to $9\frac{3}{4}$ d. This last figure represents approximately the present market-value. The quotations had to be raised proportionately.

The exports from Ceylon have slightly receded in 1902. They were:

	in 1902	1 294 750 lbs.
against	„ 1901	1 430 168 „
	„ 1900	1 409 050 „
	„ 1899	1 478 756 „
	„ 1898	1 365 917 „
	„ 1897	1 182 867 „

The figures for the various countries were as follows: —

to the	United Kingdom . . .	556 096 lbs.
„ „	America	538 970 „
„ „	Germany	146 518 „
„ „	Australia	26 408 „
„ „	China	17 115 „
„ „	France	2 376 „
„ „	Singapore	1 867 „
„ „	India	5 400 „
Total		1 294 750 lbs.

The low value of the article has lately, unfortunately, again led to numerous and very peculiar adulterations, such as have never been observed before.

In our Report of October 1899, page 23, we mentioned already, that citronella oils are met with in commerce, which, although they are unadulterated, yet do not form a clear solution with 80 per cent. alcohol, and therefore do not pass Schimmel's test. But we then said that oils which only just formed a cloudy solution, and with which no oil-drops are separated out from the solution, could not be considered objectionable, as the insolubility could only be attributed to the resinification of the (light) sesquiterpene present in citronella oil; on the other hand, it should be absolutely insisted upon, that on prolonged standing no small drops of mineral or fatty oil are separated out from the alcoholic solution, neither at the surface, nor on the bottom of the vessel.

Since then we have very rarely been in a position to examine such insoluble, but unadulterated oils. The majority of the oils characterised by insolubility was adulterated; for this reason, we had no occasion to depart from the condition imposed by us, that citronella oil must form a clear solution even in 10 volumes 80 per cent. alcohol.

Parry¹⁾ has subsequently called attention to the fact, that the oils whose insolubility in 80 per cent. alcohol must be attributed to a high

¹⁾ The Chemist and Druggist 59 (1901), 142; compare Report October 1901, 17.

content of sesquiterpene, dissolve clear, or at most with a very slight turbidity, in 81 to 83 per cent. alcohol, whilst with oils which have been mixed with only very small quantities of petroleum, the turbidity does not diminish even when 85 per cent. alcohol is used.

But along with the gradual decline in the price of citronella oil there was a great increase in the number of insoluble oils which were submitted to us for examination, and we found that even the somewhat stronger alcohol recommended by Parry did not regularly suffice for solution. The oils differed from unadulterated oils barely in specific gravity, but little in rotatory power, most in the index of refraction which was essentially lower than otherwise. Now, when in a specially striking case a rather large sample was placed at our disposal, we determined the physical constants of the portion insoluble in 80 per cent. alcohol. We found: d_{15}° 0,8411; α_D — $11^{\circ} 21'$; n_{D20}° 1,46872. The separated insoluble oil did not dissolve in 10 volumes 90 per cent. alcohol, but made a cloudy solution with about 8 volumes 95 per cent. alcohol. In order to obtain further data, a part of the original oil was carefully fractionated with water vapour; for the two fractions first passing over we ascertained the following constants:

	d_{15}°	α_D	n_{D20}°
I	0,8145	— $19^{\circ} 6'$	1,44741,
II	0,8278	— $21^{\circ} 24'$	1,45371,

whilst a pure Ceylon citronella oil taken for comparison, and reduced into fractions of equal quantity, gave the following figures for the more volatile portions:

	d_{15}°	α_D	n_{D20}°
I	0,8599	— $50^{\circ} 44'$	1,47058,
II	0,8608	— $48^{\circ} 46'$	1,47156.

It follows that to the citronella oils which do not pass the solubility-test, a comparatively highly volatile body, of very low specific gravity, and an exceptionally low index of refraction, has been added. It is open to doubt, whether it is here a question of adulteration with a fraction of petroleum or petroleum ether, or of the addition of resin spirit. Parry and Bennett who simultaneously with us made similar observations on adulterated citronella oil, and who have already published these¹⁾, are inclined to believe that it is a question of adulteration with resin spirit, without, however, giving proofs, which in any case it would be very difficult to supply. In a short time we shall have an abundance of material for examination, and we hope then to be able to clear up this question to some extent.

¹⁾ The Chemist and Druggist 62 (1903), 88.

It follows from the foregoing that from an oil adulterated in such manner, the adulterant can be separated by fractional distillation, and detected by its physical constants. For this reason Parry and Bennett, in a communication¹⁾ published shortly before the closing of our Report, propose the following standard: that the first fraction, consisting of 10 per cent. of the oil under examination, distilled under reduced pressure (20 to 40 mm) must have a specific gravity not below 0,858, and a refractive index, at 20°, not below 1,4570, and further, that citronella oil must dissolve either clear, or at most with the slightest opalescence, in 10 volumes of 80 per cent. alcohol at a temperature of 20°.

We can only express our complete agreement with this proposal. The solubility-test in 80 per cent. alcohol (Schimmel's test) must be maintained, although it may perhaps be suitable to change the temperature of 15° originally proposed by us, into one of 20°; the distillation-test will make it also possible to identify those oils, which, being but slightly adulterated, have passed the solubility test.

Under the designation "Java lemon olie" we have lately received several samples of oils, which can neither pass for lemongrass nor for palmarosa oil, and which should rather be considered as a kind of citronella oil, although they slightly differ from the latter in the odour. The mother-plant from which this oil is obtained, is presumably a species of *Andropogon*: we know nothing definite about this, but will endeavour to ascertain further details of the origin of this oil.

The samples obtained from different sources show a fair amount of similarity in their constants, as will be seen from the following short table:

d_{15}°	α_D (in 100 mm tube)	n_{D20}°	Total content of $C_{10}H_{18}O$
0,8889	+ 13° 26'	1,46466	49,09 %
0,8914	+ 10° 6'	1,46684	50,9 "
0,8809	+ 14° 52'	1,46496	49,18 "

The oils dissolve readily in 80 per cent. alcohol, but when the concentrated solution is diluted, turbidity occurs uniformly. To all appearances they do not contain geraniol, but this statement is subject to further verification, as in every case we have only had small samples at our disposal, and therefore were unable to make a thorough examination.

From the sample mentioned last we have isolated the aldehyde contained in it, by shaking with bisulphite solution. In the odour it completely resembled citronellal, whose physical constants it also possesses: boiling point 205° to 208°, d_{15}° 0,8567, n_{D20}° = 1,44791; but it was found to be *lævogyrate*, as we observed α_D = - 3°. This

¹⁾ The Chemist and Druggist 62 (1903), 408.

is consequently the first time that l-citronellal has been detected as a constituent of an essential oil. The melting point of the semicarbazone which was produced for the further identification, and was prepared according to Tiemann's directions, was found at 74° .

In the portions of the oil which did not react with bisulphite solution, cineol could be detected with certainty; they probably also contain limonene, or a mixture of limonene and dipentene.

A sample of citronella oil which takes about an intermediate place between Ceylon and Java citronella oils, was received by us some time ago from the Government Laboratory in Jamaica. We found for this oil: $d_{15} = 0,8947$, $\alpha_D - 4^{\circ} 16'$, and $n_{D20} 1,47098$. It also showed a low acid number, and contained 86,4 per cent. total $C_{10}H_{18}O$, with a citronellal-content of 25,43 per cent.

In a note appearing in the "Tropenpflanzer"¹⁾ we find that in the Botanical Garden at Victoria in the Cameroons, under the name *Andropogon citratus*, a species of grass is cultivated, which, according to an examination by Strunk, yields an oil which is seemingly identic with citronella oil. Strunk distilled 10 kilos of the fresh grass with water, and obtained a yield of 0,38 per cent oil. With the primitive means at his disposal he was able to ascertain that this oil contains about 15 per cent. of an aldehyde, which appears to be identic with citronellal.

According to the foregoing the grass cultivated at Victoria, of which it had not hitherto been possible to determine the species as the plant never reached the flowering stage, may possibly be identic with *Andropogon Nardus* L., which in the East-Indies is cultivated on a large scale for the production of citronella oil.

It has repeatedly attracted our attention, that when it is a question of their origin, the *Andropogon* grasses are frequently confounded with each other. The thought which first occurs is, that such confusion is caused by the omission of the name of the author after the designation of the species. But this does not apply in every case, for there are some exactly-defined species indicated as the mother-plants of oils which, according to our information, could not possibly be produced from them. We will give some examples of this. Tschirch, in his work "Indische Heil- und Nutzpflanzen"²⁾ mentions on page 128 *Andropogon Schoenanthus* L. as the mother-plant of lemongrass oil. The same statement is made in the chapter *Gramineae* edited by Hackel, in Engler and Prantl's "Natürlichen Pflanzenfamilien"; the oil obtained from it is said to be met with in commerce as

¹⁾ Volume 7 (1903), 37.

²⁾ Berlin 1892. R. Gaertner.

"lemon oil". Sadebeck¹⁾ also states, that *Andropogon Schoenanthus* L. is cultivated in some parts of East Africa, and that the fragrant lemongrass oil is distilled from it. But at the same time he mentions also, that this oil is used for adulterating rose oil, and thereby (and also by referring to the synonymous words rusa, palmarosa, or Turkish geranium oil) he identifies it with palmarosa oil. Finally, the annual report of the Buitenzorg botanical gardens also mentions *Andropogon Schoenanthus* L. (sereh) as the mother-plant of lemongrass oil.

With reference to a lemongrass oil from Jamaica which is said to be distilled from this species of grass, see under "lemongrass oil".

Clove Oil. Since our Report of October 1902, the prices of Zanzibar cloves have gradually advanced by a few marks per 100 kilos, until about the end of January last the rise came to a stop, and the value even declined again little by little to about the October-level. The present state of the prices may be designated as normal, healthy, and there can be no objection to the laying in of an abundant supply of clove oil.

In our new factories we have made extensive arrangements for the distillation of cloves on the largest scale, in the true sense of the word. The establishment of a private custom-house in our factory-buildings is a great advantage in this connection, as cloves and all other spices may be distilled free of duty if under control of the Customs' officers, a control which extends to the denaturalising of the spice after distillation.

The following statistics, taken from official Consular reports in the "Deutsches Handels-Archiv", may be found interesting.

Cloves. The exports were: —

	Weight in pounds:	Value in rupees:
in 1898	10856566	2155956
„ 1899	16593340	2958487
„ 1900	11788095	2372227
„ 1901	11962069	2465373

They were made up as follows: —

	1898	1899	1900	1901
		Weight in pounds:		
Europe . . .	4138086	8028780	5235388	4470632
America . . .	729960	648970	719600	252000
Asia . . .	5912800	7599517	5769293	7081471
Africa . . .	75720	316073	63814	153966
		Value in rupees:		
Europe . . .	797375	1394217	1031952	888110
America . . .	149402	110108	150079	50700
Asia . . .	1194032	1397837	1177754	1496053
Africa . . .	15147	56425	12442	30510

¹⁾ Die Culturgewächse der deutschen Colonien. Jena 1899, p. 247.

It will be seen that the exports to India have increased considerably, those to Europe slightly, whilst the exports to America have greatly gone down. As regards the European ports, the exports were in detail: —

	1899	1900	1901
Weight in pounds:			
Rotterdam	4 473 240	2 674 160	2 330 764
London	1 432 475	1 404 968	1 841 493
Marseilles	292 215	217 000	133 000
Hamburg	1 249 850	715 260	125 720
Value in rupees:			
Rotterdam	786 212	537 810	466 168
London	254 852	274 520	364 955
Marseilles	51 229	49 800	25 200
Hamburg	204 267	122 912	23 220

London, which at one time was the principal port for clove-exports, has therefore improved its position in the year under review. Rotterdam has, however, still an advantage of half a million pounds.

Clove-stems were exported: —

in	1898	1899	1900	1901
Weight in pounds:				
to Europe	584 640	3 605 245	1 743 426	1 290 868
„ Asia	305 561	216 484	220 447	210 140
„ America	336 875	555 940	98 000	140 000
Value in rupees:				
„ Europe	24 055	104 351	70 453	66 556
„ Asia	14 845	6 748	11 621	13 350
„ America	19 657	31 708	7 700	10 600

The export to Europe was shipped: —

in	1898	1899	1900	1901
Weight in pounds:				
to Hamburg	456 890	2 980 110	1 478 226	1 212 668
„ London	74 900	370 335	83 160	33 700
„ Marseilles	38 850	179 900	28 000	31 500
„ Rotterdam		unknown		112 000

In our April Report of last year, on page 24, we stated that, according to our observations, among others benzoic acid was also contained in clove oil, and we pointed out that it was probably present in the oil, if only in minute quantity, in the form of its methyl ester. We were namely able to isolate this ester from the first runnings though not in a perfectly pure state, by frequently repeated fractional distillation, and subsequent suitable treatment of a fraction which came under consideration for this body on account of its boiling point. The first portions of the oil passing over between 40° and 94° (8 to 9 mm), distilled after treatment with bisulphite solution between 161° and 220° . The first of these fractions, boiling at 161° to 165° , was tested for pinene, but yielded no solid nitrosochloride; similarly, no solid terpene

derivative could be obtained from the subsequent fractions, which, judging by their physical constants and the odour, consisted chiefly of terpenes. The constants of the two fractions distilled over sodium were as follows: 1. boiling point 165° to 170° , specific gravity 0,8567, optical rotation $-2^{\circ}31'$ (50 mm), and 2. boiling point 170° to 180° , specific gravity 0,8631, optical rotation $-1^{\circ}11'$ (100 mm). The oil passing over at 180° to 210° served for the isolation of the benzoic ester. It was oxidised at ordinary temperature with a 1 to 2 per cent. solution of potassium permanganate, until the violet colour of the solution, which was gradually added to the oil in small quantities, remained unchanged. In this manner we obtained a liquid which had a distinct odour like methyl ester of benzoic acid, and boiled at 190° to 200° , and which, being slightly lighter than water, would still contain considerable quantities of foreign admixtures. As in spite of this the saponification number was comparatively high (101,1) it was obvious that the oil had a high ester-content. By repeated careful fractionating we endeavoured, but unfortunately without success, to separate from it a fraction with a still greater ester-content. In consequence of paucity of material we were then compelled to abandon further attempts to produce it in the pure state, and to content ourselves with having proved that as a matter of fact an ester of benzoic acid was present in the oil. The saponification yielded a pure white acid crystallising in leaflets, which had the melting point 121° , could readily be sublimed, and showed all the properties of benzoic acid. When heated with methyl alcohol and concentrated sulphuric acid, it formed methyl ester of benzoic acid with its characteristic odour. We would still point out that the boiling point of the ester fraction in question very closely approaches that of methyl ester of benzoic acid (199°). By means of saponification we succeeded in identifying the compound, which was present along with the ester, as methyl heptyl ketone. The oil driven off with steam from the saponification liquor, possessed a refreshing rue-like odour. The boiling point was at 191° to 196° . The capacity of reacting with bisulphite liquor, and of forming a semicarbazone with semicarbazide in acetic solution, showed that the body was a ketone, or an aldehyde respectively. The semicarbazone melted at 118° to 119° , and when submitted to elementary analysis gave values corresponding to those of the semicarbazone of methyl heptyl ketone.

1. 0,1606 g of the substance yielded 0,3530 g CO_2 and 0,1448 g H_2O .
2. 0,1510 g " " " " 0,3321 g " " 0,1401 g "

Calculated for $\text{C}_{10}\text{H}_{21}\text{ON}_3$:

Found:

C	60,30 per cent.	59,94 per cent.;	59,98 per cent.
H	10,55 " "	10,15 " "	10,31 " "

The methyl heptyl ketone produced for the purpose of comparison by heating a mixture of calcium caprylate and acetate, yielded a semi-carbazone of the same melting point. A mixture of the two semi-carbazones melted at 118° to 119° , a proof that both bodies were identical, and that the product isolated from clove oil was methyl heptyl ketone. The presence of this ketone in oil of cloves is all the more interesting, as it had up to the now only been found in rue oil¹⁾. When the opportunity arises we will return to this body, and then identify it further. According to our present observations methyl heptyl ketone reacts with some difficulty with sodium bisulphite. To this may possibly be attributed the fact that we detected the ketone of clove oil in fractions which had already been shaken with bisulphite liquor.

In our last year's April Report²⁾ we discussed a new method (published by Verley and Bölsing) for the quantitative estimation of alcohols and phenols, which is based on this, that the alcohols (or phenols) in question are esterified in the presence of pyridine by means of a known quantity of acetic anhydride, and the acetic acid not thereby combined is titrated back. As the method was specially recommended by Verley and Bölsing for the determination of eugenol in oil of cloves, we have taken this particularly into consideration in testing the process, and have examined on the one hand eugenol mixtures of known content, on the other hand numerous clove oils, both by this method and by the one introduced by Umney. We desire to state here that some considerable time ago we slightly modified Umney's method to this extent, that, instead of a 10 per cent. potash liquor for extracting the clove oils, we use a 5 per cent. soda-solution. The results thereby obtained are perfectly satisfactory.

As contrasted with this, the experience obtained by us with the acetylation-method proposed by Verley and Bölsing is unfortunately such, that we are unable to confirm the statements made by these gentlemen as to the reliability of their method. Already with the artificial mixtures very important differences could be observed as compared with Umney's method, differences which became even more pronounced with the natural clove oils.

It should be mentioned here particularly, that we, of course, paid the most scrupulous attention to the conditions of temperature, and that the errors observed cannot therefore be attributed to this. The

¹⁾ Report April 1901, 52. — Berichte der deutsch. pharm. Ges. 11 (1901), 3.

²⁾ Report April 1902, 24.

following table which contains some of the results obtained by us, may serve as an illustration of the foregoing:

	Eugenol-content	
	according to Umney (5 per cent. NaOH)	according to Verley and Bölsing
Mixture with 10 per cent. eugenol	9,5 per cent.	13,2 per cent.
" " 50 " " "	49,5 " "	51,33 " "
" " 75 " " "	75,0 " "	73,58 " "
Pure eugenol	100,0 " "	102,3 " "
English oil of cloves	90,5 " "	79,94 " "
" " " " " "	73,0 " "	74,12 " "
" " " " " "	80,0 " "	69,53 " "

These few examples may already suffice to justify our unfavourable opinion on the method proposed by Verley and Bölsing. It is all the more surprising that we have not arrived at approximately as satisfactory results as Verley and Bölsing, as they used normal liquor for titration, but we only semi-normal solution. Further, it is not quite clear on what grounds Verley and Bölsing made the statement, that in the case of differences between Umney's method and theirs, the latter should always be preferred; for they themselves admit that with artificial mixtures Umney's method also gives figures which agree most satisfactorily. The fact that the results obtained by their method agree with those of the process recommended by Thoms is not at all convincing, as the latter gives approximate values only when the conditions mentioned in the directions are carried out most accurately — a matter which is very difficult to accomplish. For practical purposes moreover this method generally takes up too much time.

After all we still believe that the method proposed by Umney, modified by us in the above-mentioned manner, is the most practical and reliable method for the determination of eugenol. According to this process, 10 cc oil are shaken for a considerable time with a 5 per cent. soda liquor in a burette or cassia flask, and the mixture then left standing, but the vessel is occasionally turned lightly round on its vertical axis in order that oil drops adhering to the sides of the glass may also rise to the surface. The portions of the oil which have not combined with alkali are estimated volumetrically, and the eugenol-content is ascertained from the difference between the original quantity of oil and the non-phenols. In order to avoid all misunderstanding we would point out, that we can only guarantee the eugenol-content of oils of clove on the basis of the method just described. Further, we wish to call particular attention to the fact that it is here a question of percentages by volume, although with normal oils of clove the difference between percentages by weight and by volume should not be very large.

H. von Soden and W. Rojahn¹⁾ have been able to isolate from the hydrocarbons of an oil of clove stems, naphthalene²⁾, a body which up to now had not been detected as a constituent of an essential oil.

Oil of Copaiba. Oil of copaiba has been adopted officially only by the British Pharmacopœia, and it is there required to have a specific gravity of 0,900 to 0,910, lævorotatory power, and solubility in an equal volume of absolute alcohol. The degree of lævogyratation is not given, but in the article "Copaiba", i. e. copaiba balsam, it is stated that the essential oil, contained up to 40 per cent in the balsam, must have a rotatory power of -28° to -34° . That this condition is evidently due to an error is a matter to which F. W. Short³⁾ has first called attention; Parry, as appears from a recently published communication⁴⁾ by him, is also of opinion, that many oils of copaiba, although unadulterated, do not possess such a rotatory power. According to our own experience, the extreme limits within which the rotatory power may fluctuate, should be taken as -7° and -35° .

But, according to Parry, much adulterated copaiba balsam has, especially in recent times, been placed on the market, from which either a dextrogyrate (up to $+28^{\circ}$) oil is obtained, or one which is very strongly lævorotatory (-50° to -60°). If such oils are to be judged, it may always be taken for granted that they are adulterated; the change in the rotatory power in the first-named case would lead to the conclusion that so-called African copaiba balsam had been added, whilst in the second case it might be assumed that gurjun balsam had been mixed with the material used for distillation. Oil of gurjun balsam, also called East Indian copaiba oil, would no doubt, when added to copaiba oil, raise the latter's specific gravity, whereas the oil of African copaiba reduces the solubility in absolute alcohol required by the British Pharmacopœia.

Cypress Oil. In the cohobation of the distillation waters there is here also obtained a very volatile, yellow-coloured distillate, in which can be detected without difficulty methyl alcohol, diacetyl, and furfural, bodies which have already been found repeatedly in distillation waters. They were identified in the usual manner: methyl alcohol by the acid oxalate; diacetyl was separated as monophenylhydrazone, or osazone; and furfural was recognised by its boiling point, its colour-reaction with aniline and toluidine, and was also

¹⁾ Pharm. Zeitung **47** (1902), 779.

²⁾ The same substance has been found by the authors in the essential oil from the bark of a storax.

³⁾ Pharm. Journ. **64** (1900), 54.

⁴⁾ The Chemist and Druggist **62** (1903), 332.

characterised by the melting point of its phenylhydrazone. The last-named body can also be very readily identified by the semicarbazone, which, being scarcely soluble in water, is precipitated already from a dilute aqueous solution by semicarbazide acetate. It is obtained in this manner in the form of brilliant white laminæ which turn slightly yellow when kept, especially when exposed to the light. The semicarbazone melts at 197° with decomposition.

Dill Oil. From Spain we received a sample of dill oil which had been distilled exclusively from the dill plant, and which differed in its properties in a marked degree from normal dill oil. Its physical constants were as follows: $d_{15} 0.9282$, $a_D +45^{\circ}47'$, $n_{D20} 1.49638$; it was insoluble in 80 per cent. alcohol, but formed a clear solution with about 5 volumes of 90 per cent. alcohol. Judged by the odour, the oil appeared to have a large phellandrene-content; this supposition was soon confirmed, for when the oil was tested for phellandrene in the usual manner, it gave an exceptionally strong reaction. A trial to determine the carvone-content by titration with hydroxylamine hydrochloride, showed that it amounted only to about 16 per cent.

When fractionated in vacuo, by far the greater part of the oil, (four-fifths) passed over at the boiling temperature of terpenes; it was found to be almost pure phellandrene, which perhaps still contained small quantities of other terpenes. Next followed a comparatively small intermediate fraction, which, however, had only a very faint odour like carvone. The boiling point of the residue was fairly high, and the distillate was heavier than water. As there were grounds for supposing that the dill oil might contain dill-apiol, which Ciamician and Silber have found in the oil from East Indian dill, this portion was repeatedly submitted to fractional distillation in vacuo. In this manner there was finally obtained an oil which had a faint yellow colour, and which passed over constantly between 155° and 156° , at 8 mm pressure. As it was only a question of proving whether this body actually contained dill-apiol, a small quantity of the oil was heated in a sealed tube for several hours to 160° with an alcoholic solution of sodium ethylate. The reaction-product which separated out when water was added, had a slightly higher boiling point than the crude material, and when slowly cooled it gradually solidified into a hard crystalline mass, which was dried on a tile in order to remove small quantities of liquid matter, and was then repeatedly recrystallised from dilute alcohol. As was clear from the melting point 43° to 44° of the crystals and that of their product of bromination, it was actually a question of dill-isoapiol.

When the portion containing apiol was distilled, there remained in the flask a mass with a very high boiling point, which solidified

on cooling, and which could be purified by recrystallisation from boiling absolute alcohol. This, however, is probably not a hydrocarbon, but a wax-like substance.

As dill oil is met with both free from phellandrene (our own distillates from the fruit of the dill have never given us as such a phellandrene-reaction) and also containing phellandrene, the presence of this hydrocarbon must perhaps be attributed to the fact that the oil has been distilled not exclusively from the fruit, but from both the fruit and the herb, and the phellandrene-content will vary according to the quantity of the latter.

Essential Oils, Sicilian and Calabrian.

The Imperial German Consul at Messina, Mr. Eduardo Jacob, has again, as in previous years, supplied us the detailed report on essential oils which is given below, thereby ensuring the gratitude of everyone interested in this trade. These reports are all the more valuable, as they appear in the middle of the season, and do not follow the official roundabout way by which they would only attain publicity when the season is long since past.

It will be seen from the following statistical tables of the exports of essential oils from Sicily and Calabria in the year 1902, that the export of last year has exceeded that of the previous year by 264515 kilos and 2882228 Lire.

Very rich harvests of bergamot- and lemon-fruit have made it possible for the export-trade here, to place in the year under review large quantities of oil at the disposal of foreign consumers, and the latter have shown no hesitation to make use of the favourable situation, as they were able to buy, especially lemon oil, at exceptionally low prices.

This enormous increase in the exports during last year confirms what has already been pointed out in previous Reports, viz., that the world's consumption of Sicilian essential oils, and principally of lemon oil, is constantly growing, a fact which may be calculated to put a check on any further fall in the prices of lemon oil.

Export of essential oils.

	in 1901		in 1902	
	quantity Kilos	value Lire	quantity Kilos	value Lire
a) from Messina:				
to North German Ports . . .	13676	205 140	21773	304 822
„ Austria	50648	759 720	75 280	1 053 920
„ Belgium	1368	20 520	2 225	31 150
„ Denmark	2 241	33 615	3 085	43 190
forward	67 933	1 018 995	102 363	1 433 082

	in 1901		in 1902	
	quantity Kilos	value Lire	quantity Kilos	value Lire
a) from Messina: —				
forward	67 933	1 018 995	102 363	1 433 082
to France	36 312	546 195	43 609	610 526
„ United Kingdom	211 342	3 170 130	235 108	3 291 512
„ Holland	10 392	155 880	8 345	116 830
„ Russia	9 331	139 965	10 631	146 834
„ Scandinavia	6 216	93 240	7 308	102 312
„ Spain and Portugal	1 064	15 960	1 721	24 094
„ Turkey	1 560	23 400	1 726	24 164
„ United States	266 614	3 999 210	436 566	6 111 924
„ South America	3 510	52 650	—	—
„ Australia	35 369	530 535	39 749	556 486
„ Egypt	1 313	19 695	1 672	23 408
„ Greece	360	5 400	704	9 856
„ India	625	9 375	1 330	18 620
„ Malta	60	900	—	—
„ Other countries	500	7 500	12 487	147 818
Total:	652 501	9 789 030	903 319	12 646 466
b) from Reggio: —				
to Austria	26 810	402 150	31 062	434 868
„ France	24 315	364 725	32 459	454 426
„ North German Ports	5 890	88 350	3 804	53 256
„ United Kingdom	20 663	309 945	24 032	336 448
„ Malta	200	3 000	—	—
„ United States	27 440	410 100	31 388	439 432
„ Other countries	415	6 225	2 580	36 120
Total:	105 733	1 584 495	125 325	1 754 550
c) from Catania: —				
to Austria	1 650	24 750	2 671	37 394
„ United Kingdom	350	5 250	1 715	24 010
„ North German Ports	200	3 000	—	—
„ Other countries	210	3 150	52	728
Total:	2 410	36 150	4 438	62 132
d) from Palermo: —				
to Austria	12 650	189 750	7 433	104 062
„ North German Ports	1 315	19 725	20	280
„ France	—	—	2 970	41 580
„ United Kingdom	36 410	546 150	31 535	441 490
„ United States	9 350	140 250	9 049	126 686
„ Other countries	612	9 180	1 408	19 712
Total:	60 337	905 055	52 415	733 810
Total exports: —				
from Messina	652 602	9 789 030	903 319	12 646 466
„ Reggio	105 633	1 584 495	125 325	1 754 550
„ Catania	2 410	36 150	4 438	62 132
„ Palermo	60 337	902 055	52 415	733 810
Grand Total:	820 982	12 317 730	1 085 497	15 196 958

that is to say, in the year 1902 264 515 kilos and 2 882 228 Lire more than in 1901.

The figures of the exports of the last ten years are as follows:

1893: 588334 kilos, value 9356814 L.	1898: 667293 kilos, value 9015083 L.
1894: 666740 " " 8308148 "	1899: 797145 " " 10722445 "
1895: 554191 " " 8081870 "	1900: 842246 " " 10972295 "
1896: 514067 " " 7579424 "	1901: 820982 " " 12314730 "
1897: 732092 " " 9719133 "	1902: 1085497 " " 15196958 "

Bergamot Oil. This year's distillation has left much to be desired. A much smaller quantity of fruit was worked up than in the previous year, and the oil-content also did not justify the hopes which had been entertained. It was fortunate that abroad a large proportion of the previous year's rich harvest had remained unsold, and that the demand in November and up to January was comparatively small; if there had been a strong demand, the price of this article would have risen considerably already at the beginning of the manufacturing season. In view of the above-mentioned small demand from abroad, the speculators, who at Reggio had formed a combine, were unable, in spite of the greatest efforts, to drive up the prices during the manufacturing season, and their endeavours were not crowned with success until in the course of last month a stronger demand began to assert itself on the market.

The present situation is this, that the comparatively small export has left considerable stocks of bergamot oil over for the new season, stocks which amount to fully 25000 kilos.

At the present time the bergamot-trees are already in leaf, thanks to a winter free from gales, and they justify the hope of a good harvest. If this supposition is confirmed by a rich development of blossoms and a good germination of fruit, the speculators will probably lose courage, and they may show greater willingness than hitherto to realise their holdings. For this reason there is no great belief in a further rise of the prices; on the contrary, the presumption is that in the summer months it will be possible to buy cheaper than now.

Citron Oil. S. Gulli has now published the contemplated supplement to his previous notes on citron oil¹⁾, and thereby added a valuable contribution to the knowledge of this oil. The oil previously examined by him, prepared from "*cedri*", agreed (as we wish once more to point out) in its physical constants with the oil which we had at the time under examination, but differed in a marked degree from that which Burgess had before him. The oil recently tested by Gulli, which had been made from "*cedrini*" (derived from *Citrus medica gibocarpa* or *citrea*) corresponded in its physical constants to

¹⁾ The Chemist and Drugg. 62 (1903), 22.

the oil described by Burgess. Gulli, namely, found: $d_{15}^{\circ} 0,851$, and $\alpha_D + 80^{\circ} 50'$, and for another oil also prepared from "*cedrini*", $d_{15}^{\circ} 0,850$, and $\alpha_D + 79^{\circ}$.

The author further found that the oil of sweet lemon (derived from *Citrus Limonum dulcis*) represents an excellent adulterant of citron oil, for mixtures of equal quantities of common lemon oil, or sweet lemon oil, with oil of sweet orange, possessed properties almost identic with those of citron oil. But such mixtures can immediately be distinguished from genuine citron oil by the fact that they are perfectly clear, whilst citron oil soon after preparation becomes turbid, with separation of fine white crystals of the form of small needles.

Dr. Gulli was good enough to send us samples of the two above-mentioned oils prepared by him. Unfortunately, both oils reached us in a turbid condition owing to crystals having separated out, and we are therefore unable to accept such behaviour as characteristic of citron oil alone. After removing the crystalline precipitate by filtration, we found for the *cedrini* oil: $d_{15}^{\circ} = 0,8541$, $\alpha_{D21}^{\circ} = + 81^{\circ} 7'$ and $n_{D20}^{\circ} = 1,47480$; and for the oil of sweet lemon: $d_{15}^{\circ} = 0,8579$; $\alpha_{D21}^{\circ} = + 64^{\circ} 15'$, and $n_{D20}^{\circ} = 1,47568$, whilst Gulli gives for the latter $d = 0,856$ and $\alpha_D = + 64^{\circ} 30'$. Our observations consequently agree fairly well.

But the determination of the specific gravity and the rotatory power alone is not sufficient to distinguish genuine from adulterated citron oil; this is clear from a further article on this subject by the chemists of the London Essence Company¹⁾. In their opinion, adulteration can readily be detected in the same manner as already proposed by Burgess and Child for lemon oil, viz., by separating the oil to be tested into different carefully measured fractions, and determining the physical constants of such fractions. For a sample of pure citron oil with $d_{15}^{\circ} = 0,852$, $\alpha_D = + 80^{\circ} 5'$ and $n_D = 1,4749$, the authors give the following as typical values:

Fraction	α_D	n_D	Aldehyde-content
10 per cent	$+ 85^{\circ} 55'$	1,4730	—
80 " "	$+ 86^{\circ} 5'$	1,4735	—
7 " "	$+ 16^{\circ} 30'$	1,4806	53 per cent.

The two first fractions would therefore have a higher rotatory power than the original oil, which would not be the case if the oil had been adulterated. The chemists of the London Essence Company also refer to the presence of crystals as being a characteristic of citron oil.

¹⁾ The Chemist and Druggist **62** (1903), 57.

All these notes on citron oil which have been published in recent times, have been lucidly arranged in a small pamphlet issued in January last by the London Essence Company.

If we now summarise all what has been said on the subject, we find that the varieties of citron yield oils of totally different properties; the *cedri* (as has been proved by Gulli and ourselves) yield an oil which has a somewhat higher specific gravity, and a little less rotatory power, than that from *cedrini*, whilst the latter is clearly richer in hydrocarbons.

We have also had *cedrini* oils repeatedly before us (1898/99), and we found for this oil in two cases: —

$$\begin{array}{ll} d_{18}^{\circ} = 0,8507; & \alpha_{D20}^{\circ} = +78^{\circ} 39'; \\ d_{15}^{\circ} = 0,853; & \text{,,} = +77^{\circ} 53'; \quad n_{D20}^{\circ} = 1,47519. \end{array}$$

These results agree very well with those communicated by Burgess and lately also by Gulli.

In future it will therefore be necessary to discriminate severely between these two oils, a view which is supported by S. Gulli in a recently published note on citron oil¹⁾. It is obviously desirable to maintain the name citron oil for the oil prepared from *cedri*, and in the absence of a better name, the *cedrini* oils will meanwhile have to be designated as such.

Lemon Oil. The position of this article was in September 1902 as follows: —

With the rich lemon-harvest of the winter 1901/02, the consumers abroad had during the first nine months of 1902 covered the whole of their requirements for the year, and even more, in the most abundant manner. A falling-off in the demand caused in Sicily a decline in the prices to a level which had never been reached before; this again attracted the interest of speculators abroad, who could be persuaded all the more readily that it would be well to take advantage of the situation, as the lemon oil of the previous season was good in every respect, and the oil had in the course of the summer also proved its excellent keeping qualities.

An abundant supply to the consumers abroad of the previous season's oil, at low prices, appeared all the more opportune, as the prospect of the new harvest, of the winter 1902/03, was not favourable, and much higher prices were asked for new forward oil than for old spot oil.

As a matter of fact, the result of the new lemon-harvest has been about half of that of the previous one, and as in the case of the

¹⁾ The Chemist and Druggist 62 (1903), 454.

bergamot and the orange, whose yield of oil was only small, the lemon also showed a lower oil-content, as compared with other years.

If, in spite of this, the prices of lemon oil have up to now remained comparatively low, the reason of this must be found in the fact that buyers abroad, who were abundantly supplied with the previous year's product, have sent in new orders only on a small scale, and this has rendered the accumulation of a certain stock of new oil possible.

The following statistics of the export will supply the proof of this:

Export Season:

1901/02		1902/1903	
December 1901	96985 kilos	December 1902	73440 kilos
January 1902	132509 „	January 1903	95975 „
February 1902	74056 „	February 1903	97846 „

The stock held at Messina in December made it possible for the exporters to fulfil their obligations also in January and February, without having to fall back on the daily supplies of lemon oil.

The exports of last month, however, have almost exhausted the available stocks, and the export-trade can from now only rely on the quantities offered from day to day.

But, as experience shows that at Messina a considerable shortage for forward deliveries at late dates is the rule, and as moreover the consumption has not yet covered its requirements for the next nine months, whilst on the other hand the manufacturing season will come to an end at an early date on account of lack of fruit, and the stocks held by manufacturers and speculators probably amount to no more than one fourth of the previous year's stocks, there can be little doubt that an improvement in the prices within a not very distant time may be expected.

Of what importance such improvement may be, cannot at this moment be said with any certainty; it depends upon the extent to which buyers abroad have to rely on the market here until the time of the next harvest, and also upon the expectations for the season 1903/4 which will be raised by the development of the new blossoms.

The following compounds have been found up to the present in lemon oil, excepting bodies which are not volatilisable by steam, viz., pinene, camphene, phellandrene, limonene, methyl heptenone, octyl and nonyl aldehydes, citronellal, terpineol, citral, linalyl and geranyl acetates and a sesquiterpene. On removing by distillation in vacuo the hydrocarbons of a low boiling point, i. e. pinene, camphene, phellandrene and limonene, with which pass over also methyl heptenone and partially the fatty aldehydes and the citral, and on separating then by steam-distillation the volatile from the non-volatilisable constituents, a concentrated lemon oil is obtained, showing a lævorotation,

unlike the rather strongly dextrogyrate raw material. This lævorotation has always been considered as particularly characteristic for terpeneless lemon oil, indeed a rotation of at least -7° to -8° was insisted upon for this preparation.

Among the compounds met with in concentrated lemon oil are optically active only citronellal, terpineol, linalyl acetate and the sesquiterpene, the latter being known to rotate, though not in which direction; of these bodies citronellal is dextrogyrate, whereas terpineol and linalyl acetate turn the polarised light to the left, the former doing so less than the latter. The content of terpineol and linalyl acetate in concentrated lemon oil is not very considerable and it may therefore be safely supposed that the lævorotation caused by these bodies is at least counterbalanced by the dextrogyration of the citronellal, the likely consequence being optical inactivity or even slight deviation to the right.

These reflections lead forcibly to the conclusion that the lævorotation, claimed up to the present so persistently for terpeneless lemon oil, must be attributed exclusively to its sesquiterpene-content.

However, if lemon oil is freed from its terpenes, in order to increase its solubility and prevent certain troubles, it is but logical to remove also the sesquiterpene, same impeding likewise the solubility of lemon oil. But on separating the sesquiterpene a concentrated lemon oil is obtained, the properties of which differ from those required up to now for terpeneless lemon oil, the most remarkable event being the changed rotatory power.

Terpeneless lemon oil, in the true sense of the word, will always be lævograte, whereas oils freed from terpenes and sesquiterpene should be either optically inactive or slightly dextrogyrate. It will indeed soon be found in practice that the sesquiterpeneless preparation deserves the preference, for it is already soluble in about 6 to 10 parts 60 per cent. alcohol, whereas terpeneless oil requires often twice as much if not more of 70 per cent. alcohol.

On this occasion we ascertained the sesquiterpene of lemon oil to belong to the category of the light sesquiterpenes, its physical constants being: — boiling point 125° to 127° (8 mm pressure); $d_{15} = 0.8843$; $\alpha_D = -42^{\circ}$ and $n_{D20} = 1.49034$. So far we have not succeeded in obtaining crystallised derivatives by means of which this hydrocarbon might be identified.

Mandarin Oil. It is well known that a few years ago H. Walbaum¹⁾ succeeded in identifying in our laboratory the fluorescent constituent of oil of mandarin peel as methyl ester of methyl anthranilic acid. E. Charabot²⁾ has recently found that the same body is

¹⁾ Report October 1900, 31. — Journ. f. pract. Chemie II. 62 (1900), 135.

²⁾ Compt. rend. 135 (1902), 580.

present in far greater proportion, viz., up to about 50 per cent., in the oil from mandarin leaves, so that this oil may be considered as the natural source of this important perfume. The oil examined by Charabot, which had been obtained by steam-distillation from the leaves of the mandarin tree, turned the plane of polarised light $+6^{\circ}40'$; the saponification number was 160. The ester was detected and isolated by Walbaum's method. Its melting point lay at 19° . The compound was recognised as methyl ester of methyl anthranilic acid by elementary analysis, and by the acid of the melting point 179° occurring during saponification, which showed all the properties of methyl anthranilic acid.

Mandarin Oil "Schimmel & Co." This product, prepared in accordance with our German Patents Nos. 122 568 and 125 308, enjoys already a considerable amount of favour. It is chiefly used for aromatising high-quality confectionery and bonbons.

With regard to the physiologico-chemical behaviour of methyl ester of methyl anthranilic acid, which represents the most characteristic constituent of mandarin oil, interesting experiments are mentioned on page 121, which experiments prove that this substance is tolerated by warm-blooded animals in large doses without the slightest injurious effect.

Oil of Orange, sweet. As predicted, the conditions for the manufacture of this oil during the present season were very unfavourable. The orange-harvest did not everywhere give satisfactory results, and was particularly poor in those districts, whose fruit, as compared with that of other districts, is characterised by low keeping-qualities, and which is therefore chiefly used for working up into orange oil. Nevertheless, a good oil-content was anticipated, and sales for forward delivery were being made on the basis of about 11,50 marks per kilo cif. Trieste.

But the first pressing trials already proved that the oil-content was very low, and that the manufacture at the above-mentioned price was bound to result in loss. The manufacture of orange oil was therefore not commenced with the usual energy, but was only started with a limited number of hands.

A very brisk export-trade in fruit in cases, and the year by year increasing number of whole truck-loads sent to the Upper Italian markets, absorbed moreover a greater quantity of fruit for purposes of consumption than at other times, so that the owners of orange-gardens, in spite of the attractive prices of orange oil, yet found it more advantageous to sell the fruit for consumption than to supply it to the manufacturers for expression.

We are therefore now face to face with a very small production, and the stocks still in hand may possibly at this moment not exceed 5000 to 6000 kilos. Nobody will therefore be surprised by a further increase of the prices beyond their present level.

The manufacturing season now lying behind us has been extremely interesting, as it has brought to the light various anomalies respecting the chemico-physical constants of the different oils.

Rarely has in previous years the effect of the atmospheric conditions during the ripening period of bergamots, oranges and lemons, come so prominently into relief, as in the half-year just closed. A matter which is specially striking, is the poor content of essential oil of all the various *Citrus* fruits.

Orange oil showed on the whole a higher specific gravity than hitherto; sweet Sicilian oil had a lower rotatory power than in previous years, but sweet Calabrian oil, on the other hand, a higher rotation. Oil of bitter orange had a strikingly high specific gravity — both in Calabria and in Sicily, — the average being 0,854 to 0,856; the Calabrian oil had a normal rotatory power, but the Sicilian an exceptionally low rotation.

Various differences, as compared with previous years, could be detected in lemon oils from certain districts which are subject to other climatic conditions than the district adjoining the Strait of Messina, particularly the one on the average higher specific gravity of this year's lemon oil in most of the producing districts of the island, with exceptionally low gravity in some others.

With regard to the prospects of the coming harvest, nothing can as yet be stated with certainty. The smaller crop of last season, and the fact that the trees (which are already in full foliage) have been brought into an excellent condition by copious rainfall during the winter, justify the supposition that the next harvest will have good and abundant results if no unfavourable weather-conditions occur during the flowering season.

But good harvests are most necessary, as in the opposite case, in view of the low stocks of all these oils, the prices of all the various kinds would harden rapidly, and the market during the next nine months would be exposed to disagreeable and trade-disturbing fluctuations.

Eucalyptus Oil. 'Globulus' oil is at present very scarce and quoted higher. Algerian sellers have not carried out their contracts, and the chances for the Australian product are consequently more favourable. The 'Amygdalina' quality containing phellandrene is abundantly in stock.

J. H. Maiden has again supplied some contributions to the knowledge of the eucalyptus species, to which we can here refer only briefly, as they are essentially interesting from a botanical point of view. In the first place we would mention a work on *Eucalyptus Behriana* F. v. M.¹⁾ in which are discussed the characteristic differences between that species of eucalyptus and *E. hemiphloia* F. v. M., *E. populifolia*, *E. largiflorens*, *E. odorata* and *E. incrassata* var. *dumosa*.

A further short work deals with *Eucalyptus Macarthuri* D. and M., whose presence in Tasmania is confirmed. As this species of eucalyptus presumably will become important on account of the oil it yields, which is rich in geranyl acetate, Maiden recommends that the trees, in the interest of the oil distillation, should not be felled, but that only the branches should be cut off.

In the long list of Australian useful trees²⁾ the author also mentions *Eucalyptus haemastoma*, *E. haemastoma* var. *micrantha*, and describes these along with *E. punctata* D. C. which is frequently mistaken for the *grandiflora*-kind of *E. resinifera*, and is popularly known as *Grey gum*.

Treatises by the same author, on *E. Baueriana* Schauer and *E. calycogona* Turcz., are found in the Proc. of the Linn. Soc. of N. S. W. 1902, Vol. II, and on *E. tereticornis* Smith and *E. rostrata* Schlechtendal, in the Bulletin de l'herbier Boissier, 2^d series, 1902.

We desire to avail ourselves of this opportunity, to call the attention of those of our readers who take an interest in the extraordinarily varied family of eucalypts and in the essential oils obtained from their individual species, to the recently published work by R. T. Baker and H. G. Smith: "A research on the eucalypts especially in regard to their essential oils."³⁾

Both authors have now for a long time been connected with the Sydney Technological Museum, the first chiefly as botanist, the other as chemist, and they have occupied themselves particularly with a thorough examination of the family of eucalypts, and, indeed, their names have been repeatedly mentioned in these pages in discussing their previous work.

The present work, which is provided with very good habitat-pictures, and also illustrations of branches of the individual species with the organs which are the most important for the identification and differentiation, represents an epitome of everything that has up to now become known of eucalypts, both from a botanical and a chemical point of view. The fact that the authors have on this occasion taken their

¹⁾ Trans. of the Royal Soc. of South Australia 1902.

²⁾ Agricultural Gazette of N. S. Wales, 1902.

³⁾ Sydney, 1902.

own researches specially into consideration, is a matter for which one can hardly find fault with them, but for this very reason it may be assumed, that the views thus set forth by them will not always meet with unanimous approval on the part of their more immediate colleagues. The discussion of the individual eucalyptus-species is conducted from the chemical point of view, i. e. according to the principal constituents present in the individual oils. This is followed by a reproduction of various works by H. G. Smith from the 'Proceedings of the Royal Society of N. S. Wales' respecting the composition and constituents of a few eucalyptus oils, and finally details are given on the method of distilling eucalyptus oils, as in vogue in Australia, which method is elucidated by well-executed pictures. The work ends with a clearly arranged table which permits ready reference to the properties and constituents of any eucalyptus oil.

This publication meets a real want, and is all the more to be welcomed, as with the large number of eucalyptus species described and the still larger number of synonyms, it was not at all, or hardly, possible for anyone who had not made a special study of this subject, to find the way in such a chaos.

Fennel Oil. We are in the pleasant position of now being able to supply our own distillate from purified Galician seed of which we have since January received every month a number of truck-loads.

Gardenia Oil. E. Parone¹⁾ has published a work on the properties and chemical composition of the essential oil of gardenia, from which we abstract the following:

The gardenia oil obtained by maceration from the fresh gardenias gathered during the flowering season, has a yellowish colour, and possesses at 20,5° the specific gravity 1,009. The specific rotation is $[\alpha]_D = +1,47^\circ$, at 20°, in a 50 mm tube. At ordinary pressure the oil commenced to boil at 204° with partial decomposition; at a pressure of from 12 to 15 mm the bulk passed over between 84° and 150°. Parone has detected the following bodies as constituents of gardenia oil: benzyl acetate, styrolyl acetate, [acetate of the methyl phenyl carbinol $C_6H_5 \cdot CH \cdot (OCOCH_3)CH_3$], linalol, linalyl acetate, terpineol, and methyl ester of anthranilic acid.

Benzyl acetate represents the principal constituent of gardenia oil, whilst the aroma peculiar to the oil is chiefly due to the styrolyl acetate.

Geranium Oil. Within the last 6 months the prices of the Algerian oil have declined to a not inconsiderable extent, and they may possibly drop still lower, as, according to our personal experience, the cultivation is now carried on on a much larger scale. A suspicious

¹⁾ Boll. Chim. Farm. 41, 489, according to Chem. Centralblatt 1902, II, 703.

fact is also this, that efforts are made to conclude contracts running over several years, which safeguard the seller but not the buyer, as, in case of a failure of the harvest, the former is covered by the "force majeure" clause, leaving the purchaser to do the best he can.

Réunion oil is at present very animated. Although prompt oil is fairly scarce and is kept still high, the prospects of the new distilling-season commencing in April appear to be favourable, and a large part of the yield has already been placed in advance at very acceptable prices.

As to ourselves, we have through our representative at St. Denis strongly participated in this favourable state of affairs, and we now quote this article considerably lower, in accordance with the average of our purchases; the following statistics show that at such an exceptionally low price no risk is incurred: —

Quotation on	1 st	April	1894,	44	marks	per	kilo
"	"	1 st	"	1895,	44	"	"
"	"	1 st	"	1896,	43	"	"
"	"	1 st	"	1897,	40	"	"
"	"	1 st	"	1898,	32	"	"
"	"	1 st	"	1899,	30	"	"
"	"	1 st	"	1900,	30	"	"
"	"	1 st	"	1901,	38	"	"
"	"	1 st	"	1902,	40	"	"
"	"	1 st	"	1903,	30	"	"

Our highest quotation was in 1891, at 48 marks per kilo. For large contracts we invite correspondence.

Spanish geranium oil, which in point of quality is not approached by any other kind, remains with the limited production an article of luxury. For certain purposes this oil is indispensable.

The prices of the Indian distillate, also called palmarosa oil, have suffered a heavy fall, in consequence of a considerably increased production combined with an absence of inclination to buy. This fall, as compared with the values of the previous season, amounts to about 50 per cent. Hitherto this oil was only distilled in Khandesh, in Bombay Presidency, but lately the production has also been taken up on the coast of Madras whence fairly considerable quantities have this year already been placed on the market via Bombay, a fact which has also influenced the prices. It may be taken for granted that this new source of supply will in future form a strong competitor, and that the prices will permanently remain low, which would promote the consumption. At the present values the article will have all the more interest for the soap-manufacturers, as the parcels which have appeared on the market were chiefly of such a fine quality as had

not been met with last year. Our very large stock consists exclusively of such.

The same is the case with gingergrass oil, which has never before been of such good quality, or so moderate in price. Efforts made to ascertain further particulars as to the origin of this oil have remained unsuccessful, and for this reason no guarantee can be given of either the origin or the uniform composition of the supplies. But in any case, the parcels at present in stock do not appear to contain foreign admixtures. We are earnestly continuing our efforts to elucidate the existing mystery, and, as has been the case with so many other products of Asia, they are bound to lead at last to the desired end.

Jasmine Oil "Schimmel & Co." The consumption of this perfume, which we were the first to produce and introduce into commerce, is constantly increasing, no matter what the result may be of the harvest of jasmine-flowers in the South of France. At the same time, the prices of the flowers may be influenced to a certain extent by the competition of the artificial oil, and it would not surprise us if an improvement of the natural products from jasmine-flowers by means of the artificial oil were found to be practical, and would become more general.

Oil of Juniper-Berries. The reports from Hungary announcing a failure of the harvest of juniper-berries, have been fully confirmed. For the first time in our long experience there has been a lack of Hungarian oil of juniper-berries, i. e., the oil which is obtained as a by-product in the "Borowiczka"-distillation. This oil is not normal, but has had the best readily soluble portions abstracted by the brandy. But when the demands are not too high, it is very useful when rectified, and under the designation "rectified" it represents the ordinary commercial quality of this article.

Normal pure distillates from berries are our two first qualities; these are distilled by ourselves from the best Italian berries, rich in aroma, and most carefully purified. This kind of berries, as is well known, is also preferred for the finest brands of geneva. We have used these exclusively this year, as Hungary had practically nothing at disposal for exportation.

Kaempferia Oil. Some time ago¹⁾ P. van Romburgh detected in the essential oil of *Kaempferia Galanga* L., ethyl p-methoxy cinnamate as principal constituent. When recently examining the liquid portions of the oil, the same author²⁾ obtained a fraction boiling between 155° and 165° (30 mm), which could be split up by saponification into

¹⁾ Report October 1900, 38.

²⁾ On some further constituents of the essential oil of *Kaempferia Galanga* L. Kon. Akademie van Wetenschappen, Amsterdam, May, 1902, 618.

cinnamic acid and ethyl alcohol, and which, therefore, consisted of ethyl cinnamate. This body, which represents almost one-fourth part of the oil, could only be separated with difficulty from a substance of nearly the same boiling point. The separation could finally be accomplished by treating the mixture with 80 per cent. alcohol, in which the bulk of the ester dissolved. The remaining portion was purified by boiling with potash, treatment with a solution of bromine in chloroform, and shaking with concentrated sulphuric acid. In this manner van Romburgh obtained an inactive, colour- and odourless liquid of the boiling point 267.5° (738 mm) and the specific gravity 0.766 at 26° , which on cooling solidified completely. By analysis and determination of molecular weight, the formula $C_{15}H_{32}$ was obtained. The only hydrocarbon of this composition known up to the present is pentadecane, described by Krafft, whose properties so closely agree with those of the body found, that the identity of the two cannot be doubted. More than half the liquid portion of Kaempferia oil consists of this paraffin.

Lavender Oil. According to the most recent reports from the departments Alpes-Maritimes and Basses-Alpes, the stocks held at first hand are practically exhausted, and the prices are almost left at the mercy of the middlemen. As a matter of fact, 19 to 20 francs has been paid for fine qualities.

In the departments Vaucluse, Hérault, Drôme and Gard, the stocks are also nil. For many years there has not been such lack of this eminently important article, and we are afraid that before the new harvest the position will come to a head in a manner never dreamt of. The whole world's requirements depend solely upon the production of the above-named departments, and these requirements, according to all indications, are incessantly increasing. Although no statistics on this subject are in existence, the enormous development of the toilet-soap industry, and the numerous specialities for which lavender oil is employed in large quantities, leave no doubt whatever on this point.

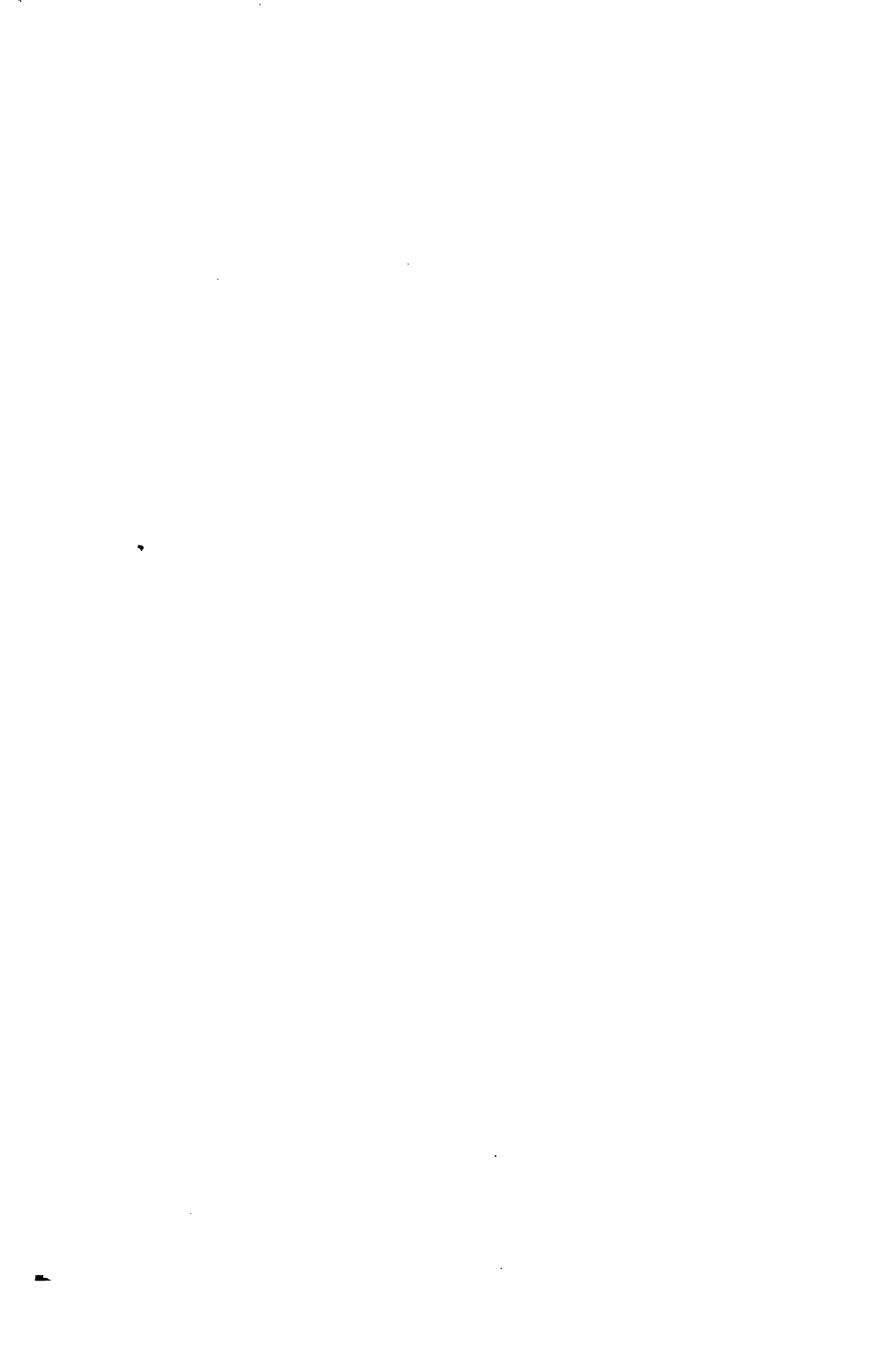
Through the good offices of Mr. Jean Gras of Cannes we are in a position to present again illustrations of some portable stills for lavender oil (Fig. 1, 2 and 3), all of which are from the district of Séderon (Basses-Alpes) which supplies good-quality oils, containing about 30 to 36 per cent. ester. These installations are situated at a height of some 3000 to 3300 feet above the sea-level; the highest point in the vicinity is the Mont Ventoux (6273 feet high). In these altitudes water is frequently scarce, so that for purposes of condensation water from tanks, or even the almost hot water running out of the Florentine flasks must be used, a method of cooling which naturally must have an unfavourable effect on the quality on the oil.



Nr. 1.



Nr. 2.



In French lavender oil there had up to now been detected: linalol; linalyl acetate, butyrate and valerianate(?)¹⁾; geraniol²⁾; pinene; cineol³⁾; and coumarin⁴⁾. By an examination which we recently again took up, we have been able to increase the knowledge of this oil by a few important bodies. We worked up 4 kilos of a genuine oil from the South of France, which had the following physical constants: specific gravity 0,8902; optical rotation $\alpha_D - 7^\circ 6'$; saponification number 116,5, corresponding to an ester-content of 40,7 per cent. linalyl acetate. In order to prevent decomposition as far as possible, we distilled in vacuo right from the beginning. Between 30° (40 mm) and 125° (5 mm) the whole quantity of oil passed over, apart from about 350 grams of a resinous residue.

With fuchsin and sulphurous acid, the first portions, boiling between 95° and 125° , showed a strong aldehyde-reaction. From this, and also from the fact that a crystalline compound was thereby obtained in minute quantity, from which sodium carbonate liberated a substance which strongly excited coughing, it may be assumed that valeric aldehyde was present in the first runnings.

Traces of amyl alcohol also appear to be present in lavender oil. For example, it was possible to obtain from the fraction boiling from 125° to 140° , with phthalic anhydride, a small quantity of a liquid boiling from 129° to 133° , which violently reacted with sodium, with formation of a colourless compound. From the latter an oil was separated off with water, which had the characteristic odour of amyl alcohol.

1-Pinene. We have once more thought it worth while to demonstrate the presence of this hydrocarbon which we had already previously detected in lavender oil. It was found without difficulty in a fraction of the boiling point 153° to 159° (72° to 75° at 21 mm), with the specific gravity 0,8641, optical rotation $\alpha_D - 6^\circ 10'$, by means of the nitrosochloride of the melting point 103° , and the nitrolbenzylamine melting at 122° .

Cineol. This body, which also had been discovered previously, was contained in a fraction boiling between 175° and 177° , and having the optical rotation $\alpha_D - 1^\circ 10'$. The iodol compound produced in large quantity, melted after purification from alcohol at 112° . The presence of the two last-named bodies in lavender oil may thus be accepted as definitely proved. Other terpenes, such as phellandrene, dipentene, and limonene, could not be detected.

¹⁾ Report April 1892, 22. — Journ. f. prakt. Chem. II. 45 (1892), 590.

²⁾ Report April 1898, 31.

³⁾ Report October 1893, 26. — Journ. f. prakt. Chem. loc. cit.

⁴⁾ Report October 1900, 40.

Ketone $C_8H_{16}O$. This substance to which in part lavender oil owes its refreshing odour, had hitherto not yet been more closely identified by its physical constants, as the production of the body in the pure state is attended with considerable difficulties. At the same time, we were able to give some details as to its boiling point and odour, and also of a solid derivative. As we suspected a ketone in the body, on account of its fruit-like odour, but as it formed no solid compound with bisulphite, we endeavoured to purify it at ordinary temperature by oxidation with a 1 per cent. solution of permanganate. The oil, freed in this manner from readily oxidisable admixtures, boiled for the greater part at 159° to 166° , and had the specific gravity 0,8445. We obtained from it a semicarbazone which crystallised from benzene in brilliant leaflets of the melting point 116° to 117° . An elementary analysis gave values which point to the semicarbazone of a ketone $C_8H_{16}O$:

0,1534 g of the substance yielded 0,3282 g CO_2 and 0,1427 g H_2O .

Found:

Calculated for $C_9H_{19}ON_3$:

C = 58,34 per cent.,

C = 58,38 per cent.

H = 10,33 „ „

H = 10,27 „ „

The ketone could therefore be the methyl hexyl, or the ethyl amyl ketone. In view of its boiling point (boiling point of the ethyl amyl ketone 164° to 166°), and of the property of not reacting with sodium bisulphite, its identity with the latter might be assumed. This is supported by the fact that the melting point of the methyl hexyl ketone-semicarbazone lies at 123° , i. e. 6° higher. A mixture of the two semicarbazones of different origin melted already below 110° , which is a proof that the derivative melting at 116° to 117° cannot be identical with that of the methyl hexyl ketone. The result obtained by oxidation with chromic acid also speaks in favour of ethyl amyl ketone. According to Wagner's¹⁾ rules regarding the progress of oxidation with aliphatic monocarbonyl ketones, the preponderating formation of caproic acid was to be expected. We oxidised whilst heating for several hours on a water bath with frequent shaking. The oily acid with the odour of valeric acid, isolated from the reaction-mixtures, yielded a silver salt which could be recrystallised from water, and whose silver-content completely agreed with that calculated for silver caproate:

I. 0,2204 g of the substance yielded 0,1067 g Ag.

II. 0,1025 g „ „ „ „ 0,0497 g „

Found:

Calculated for $C_6H_{11}O_2Ag$:

I. Ag = 48,41 per cent.,

Ag = 48,43 per cent.

II. Ag = 48,50 „ „

¹⁾ Journal für praktische Chemie II. 44 (1891), 257 et seq.



Nr. 3.



The ketone had therefore been oxidised chiefly into caproic acid. Unfortunately, ethyl amyl ketone is difficult to approach by synthetic process. For this reason, we were as yet unable to compare it, with regard to its properties, with the ketone from lavender oil. The ketone has up to the present not been detected in any essential oil, and its discovery is therefore all the more interesting. The quantity contained in lavender oil may amount to at most 0,2 per cent. In our next Report we hope to be able to supply the physical constants which are still wanting.

d-Borneol. This alcohol was isolated from fractions boiling between 85° and 92° (7 to 8 mm), whose physical constants lay between the following limits: specific gravity 0,9069 to 0,9223; optical rotation $\alpha_D - 3^{\circ} 49'$ to $-2^{\circ} 35'$; saponification number 213 to 237. The fractions were saponified with alcoholic potassa, and the alcohols of the boiling point 96 to 103 (13 mm) thereupon obtained were esterified with phthalic anhydride. From the solution of phthalic ester salt, freed from oil by extraction with ether, resulted on saponification an alcoholic mixture of a pronounced borneol odour. By fractionating at ordinary pressure a slightly dextrogyrate oil of the boiling point 205° to 220° was separated off, which did not solidify in a freezing mixture, but which, on oxidation with Beckmann's mixture, yielded large quantities of camphor. The latter was driven off with steam from the oxidation-liquid, and obtained as a solid body of the melting point 175° (after subliming). Its oxime melted at 118° to 119° . This proves the presence of d-borneol in lavender oil, and the borneol occurs in it not only in the free state, but also combined with acetic acid.

Attempts to produce the phenyl urethane of the borneol from the above-mentioned fraction boiling at 205° to 220° , were not successful, — possibly in consequence of an admixture of geraniol.

In the portions of the above-mentioned fractions which could not be esterified with phthalic anhydride, and in others of a slightly higher boiling point, we have repeatedly endeavoured to detect terpineol. Although the portions used for the examination had an odour reminding of terpineol, the latter could not be identified either as a solid body, or by means of its phenyl urethane.

Geraniol. We had previously already shown that geraniol is present in lavender oil, but up to the present it was not known whether geraniol occurs as a free alcohol and as ester, or only in one of these forms. We have now been able to prove that both forms are contained in the oil. For the purpose of detecting free geraniol, we treated a considerable quantity of oil of the boiling point 89° to 93° (6 to 7 mm) with phthalic anhydride. From the solution of the phthalate, which had been frequently extracted with ether, there resulted, after saponification, an alcohol of the boiling point 225° to 232° , which had the

unmistakable odour of geraniol. The phenyl urethane crystallising from petroleum ether in the form of needles, melted at 80° to 81° .

The fractions boiling at 93° to 94° , 94° to 103° , and 103° to 106° (7 mm), were rich in esters of geraniol; their saponification numbers were on the average 170. By repeated careful fractionating we succeeded in isolating among others a fraction of the boiling point 100° to 102° (8 to 9 mm) the specific gravity 0,9125, and the saponification number 210,6. The latter corresponds to a content of 73,5 per cent. of an ester $C_{10}H_{17}O \cdot COCH_3$. The alcohol of the boiling point 102° to 109° (8 to 9 mm) resulting from this on saponification, was recognised by the odour as geraniol. When triturated with powdered calcium chloride, it formed a solid cake. From this solid compound, purified with petroleum ether, there was regenerated with water pure geraniol of the following constants: boiling point 105° (8 mm); specific gravity 0,8825; optical rotation $\alpha_D = -0^{\circ} 2'$. The melting point of its diphenyl urethane was found at 81° to 82° .

The mixture of acids liberated from the saponification-liquors of the above-mentioned fractions, passed over between 105° and 230° . The bulk of this consisted no doubt of acetic acid, whose pungent odour was characteristic of a fraction boiling at 110° to 120° . The silver salt, however, gave figures which did not completely agree with those required for silver acetate. In spite of this, there is no room for doubt that the salt analysed represented mainly acetate of silver. The figures of the silver salt crystallising from water in well-developed needles, were as follows: —

0,3227 g of the substance yielded 0,2050 g Ag.

Found: 63,53 per cent. Ag.

Calculated: 64,67 per cent. Ag.

The difference between the value found and that required may no doubt be explained by a slight admixture of a salt with a lower silver-content. The fractions 130° to 170° , and 170° to 200° , gave values which point to butyric and valeric acids respectively. Both these acids have previously been detected by us in lavender oil. An acid boiling at 200° to 230° formed a silver salt, whose content of silver agrees with that of silver caproate: —

0,2284 g of the substance left 0,1108 g Ag.

0,2404 " " " " yielded 0,2804 g CO_2 and 0,1025 g H_2O .

Found:

Calculated:

C = 31,81 per cent.,	32,29 per cent.
H = 4,74 " "	4,93 " "
Ag = 48,51 " "	48,43 " "

According to the above-mentioned results, lavender oil contains, in addition to free geraniol, also the latter's acetic and caproic esters.

Coumarin. We have also directed our attention once more to the detection of this body which has a not unimportant bearing on the lavender odour, and which has already been repeatedly isolated by us from lavender oil. It was detected in the highest ester-containing portions of the oil, boiling at 103° to 126° (5 mm), when it was found as the distillation-residue of the acids isolated from the saponification-liquor of these fractions. After recrystallisation from alcohol it had the melting point 67° to 68° , and the characteristic pleasant odour.

Finally we would mention an occurrence which had already been observed in the first examination of lavender oil made in our laboratory. This is the simultaneous occurrence of the odour like form-aldehyde, and the formation of a gelatinous sticky substance, when fractions of the boiling point 78° to 90° (5 mm; 195° to 215° at ordinary pressure) are distilled, a fact of which we are at present unable to explain the cause.

As might be expected, our work¹⁾ on the ester-question does not meet with the approval of Mr. E. Parry²⁾. He thinks fit to dispose of this matter with some disdainful remarks, and for the rest maintains his assertions. As we have already mentioned in our previous Report³⁾ that for us the ester-question was settled once for all, there is no occasion for us to return to the subject.

Lemongrass Oil. The value of this article has undergone considerable fluctuations. The lowest point was reached in November, at 4 d. per oz., whilst at the present time it cannot be bought below $5\frac{1}{4}$ d.

The export from Cochin amounted in 1902 to only 2350 cases, but, on the other hand, fresh sources of supplies have appeared, which in the near future may possibly make competition to the present monopoly.

To all appearances the cultivation of *Andropogon* grasses in the West Indian islands, to which we referred in our last October Report, is extending. We have lately received two further samples of *Andropogon* oils from the Government laboratory in Jamaica. On one of these oils we have already reported under the heading citronella oil; the other one was, like the previous one from Antigua⁴⁾, designated

¹⁾ Report October 1902, 46.

²⁾ The Chemist and Druggist 61 (1902), 1028.

³⁾ Report October 1902, 48.

⁴⁾ Report October 1902, 50.

as having been obtained from *Andropogon Schoenanthus*, but it has such a pronounced odour of lemongrass oil, that we have no hesitation in calling it by that name. It compares favourably with the Antigua oil by its considerably higher aldehyde-content (83,5 per cent., against 48,2 per cent. for the other) but it shares with the latter its insolubility in 70 and 80 per cent. alcohol; 90 per cent. and absolute alcohol form at first a clear solution, but when more is added, they cause strong turbidity. In its physical constants the oil does not show any specially great differences from those observed at other times; we found $d_{15}^{\circ} = 0,8922$, $a_D(100\text{ mm}) = -0^{\circ} 9'$, and $n_{D20}^{\circ} = 1,48825$.

Oil of *Leptospermum scoparium*. C. E. Atkinson¹⁾ describes the essential oil of this shrub, which is called *manuka* by the natives of New Zealand, as a brown liquid having an aromatic odour and an acrid astringent taste. Its yield is but small. The physical constants are as follows: specific gravity 0,916 (12°), congealing point — 17°. It boils between 223° and 280°, chiefly about 260°.

Linaloe Oil. The supplies from Mexico in recent times have been totally insufficient, and moreover now and then of unreliable quality. The prices have advanced by several marks. The export in 1901 amounted to 12212 kilos.

Oil of Sweet Marjoram. In our Report of October 1902 we gave on page 51 an abstract from a work by Genvresse and Chablay on the constituents of oil of sweet marjoram. Shortly after the publication, Professor Genvresse wrote to us that the oil, which he had believed to be oil of sweet marjoram, was not obtained at all from *Origanum Majorana*, but from *Calamintha Nepeta*, a plant distributed in the Mediterranean countries, which also belongs to the labiates, and which in the South of France is wrongly designated as marjoram. We have now before us a detailed publication²⁾ by the two above-mentioned authors, in which they specially refer to this matter.

As we have already mentioned, calamintha oil contains a small quantity of l-pinene, a hitherto unknown ketone $C_{10}H_{16}O$, to which the name calaminthone has been given, and, in the portions boiling about 225°, pulegone. Calaminthone boils under 745 mm pressure at 208° to 209°, and at 20° has the specific gravity 0,930. The oxime produced from it melts at 88° to 89°, and in ethereal solution combines with dry hydrochloric acid gas into an addition-product melting at 165°; the melting point of the semicarbazone lies at the same

¹⁾ Pharm. Journ. **69** (1902), 369.

²⁾ Compt rend. **136** (1903), 387.

temperature. Calaminthone yields as products of reduction menthone and menthol. With the exception of the position of the double linking which still remains to be ascertained, the constitution of this ketone has thus been determined with a fair amount of certainty.

Matico Oil. Fromm and van Emster have recently published¹⁾ the results of the examination of a matico oil which originated from our factory and which was marked 'heavy portions'²⁾. This oil had the specific gravity 1,123 at 15°, and differed in a marked degree from the oil hitherto examined, by the total absence of asarone and matico camphor. About 70 to 75 per cent. passed over between 275° and 289°, and contained chiefly only one body, which the authors call matico ether, and whose formula was found as $C_{14}H_{18}O_4$. It represents a bright-yellow faintly fluorescent oil, volatilising with water vapour only with difficulty, which has the boiling point 282° to 285°, and the specific gravity 1,136 (at 17°). When kept for a prolonged time in a dark place matico ether acquires a brown colour, an occurrence which does not take place when the substance is left standing in sunlight.

Chemically matico ether behaves very indifferently. It is attacked by hydriodic acid with loss of pure methyl iodide. The methoxyl determinations after Zeisel correspond to the value of two methoxyl groups. When oxidised with a 5 per cent. solution of potassium permanganate, the new body yields a neutral product of the melting point 88°, and an acid having a melting point of 138°. The former is an aldehyde of the formula $C_{10}H_{10}O_5$, and is called by the authors matico aldehyde. With silver oxide it is oxidised into the acid $C_{10}H_{10}O_6$ maticoic acid. This is identic with the acid of the melting point 138° obtained direct by oxidation of matico ether.

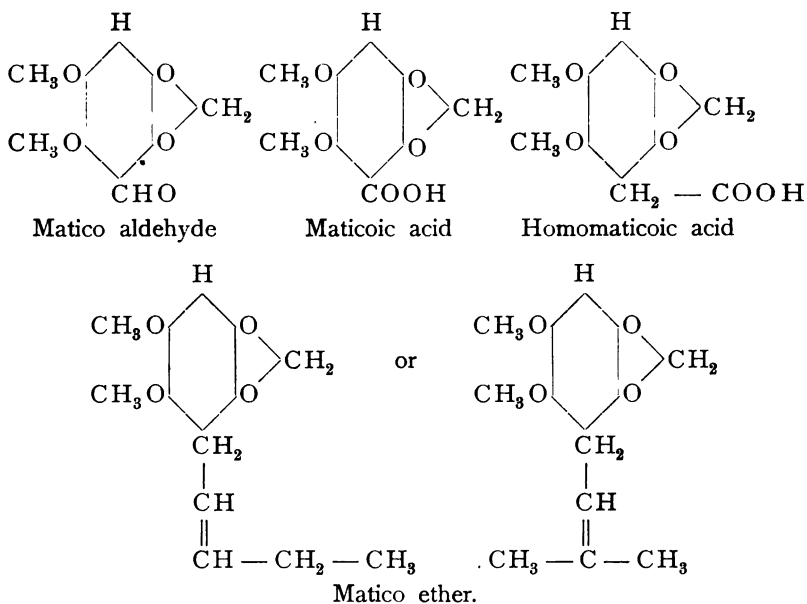
From the portions of matico oil boiling above 275°, there can be isolated by oxidation with a 2 per cent. solution of potassium permanganate, in addition to matico aldehyde, also homomaticoic acid, whose melting point lies at 96°, and to which the formula $C_{11}H_{12}O_6$ belongs. Like matico aldehyde and maticoic acid, this acid also contains two methoxyl groups.

If the fraction of the examined oil which boils above 275° (dissolved in glacial acetic acid, chloroform, petroleum ether, or carbon disulphide) is mixed with an excess of bromine, the bromide $C_{11}H_{13}O_3Br_3$ is obtained, which melts at 116°.

¹⁾ Berliner Berichte **35** (1902), 4347.

²⁾ We would point out, that it was here not a question of a normal oil, but only of the portions which during distillation had separated out on the bottom of the receiver, and which therefore were heavier than water. We have observed that oils whose distillation-material contains a large admixture of fruit heads, are comparatively richer in heavy constituents than those which have been distilled from leaves only.

The authors make a provisional attempt to harmonise the results obtained with the following formulæ:



Mustard Oil. The prices of the sorts of mustard-seed which come under consideration for the preparation of genuine mustard oil, have declined somewhat in the course of last autumn, although for example Indian mustard has not yet come back to the low level of the years 1895 and 1896. So-called mustard-cakes — the pressed-out mustard-seed which has been freed from fatty oil — were supplied in truck-loads from Russia at moderate prices. Expressed oil of mustard is used in Russia for alimentary purposes.

Mustard Oil, artificial. Since our new factory-buildings offer sufficient room to take up the manufacture of new articles, we have incorporated artificial mustard oil into our programme of manufactures. Our installations enable us in case of need to meet all competition.

We are prepared to prove this assertion by facts, and ask our friends to consider our quotations when in the market for this article.

The quality of our product naturally reaches the highest degree of perfection.

Myrtle Oil. There has been such a strong demand for the fine Spanish distillate, that we have only been able to execute the orders in part. The myrtle grows at some spots on the Riviera in enormous

quantities. This is, for instance, the case in the neighbourhood of San Remo, on the slopes of the valley leading to Ceriana, at the foot of Monte Bignone. It is surprising that no portable still has yet been put up there, but that, on the contrary, this source of supply is left absolutely unused.

Neroli Oil. In our last Report¹⁾ we published an examination of neroli oil made in our laboratory, in which we communicated the presence in this oil (not yet demonstrated by anyone else) of pinene, camphene, dipentene, terpineol, phenyl acetic acid, benzoic acid, and decylic aldehyde, and also by means of linalyl phenyl urethane (discovered by us), once more detected linalol which was already known as a constituent of the oil. A few weeks afterwards a work on neroli oil by A. Hesse and O. Zeitschel²⁾ was also published, in which they confirmed both the presence of camphene and terpineol, and also that of linalol, geraniol and linalyl acetate, bodies whose presence as constituents of this oil had first been communicated by Tiemann and Semmler³⁾.

Hesse and Zeitschel in their publication⁴⁾ call our examination of neroli oil a "preliminary communication", which was to be followed by a "publication". We are bound to protest against this misleading and wholly unwarranted description of our publication. The facts rather are these, that through our earlier publication, Hesse and Zeitschel had been placed in the position that they could only confirm a part of our results. A rectification of this matter has just appeared in the "Journal für praktische Chemie"⁵⁾. In the same work the supposition put forward by Hesse and Zeitschel, that the neroli oil examined by Tiemann and Semmler had been largely adulterated with petitgrain oil, and that consequently their work in this connection was of no importance for the knowledge of the composition of neroli oil, was rejected as not substantiated.

Indol, which had hitherto only been detected by P. Engels⁶⁾ in neroli pomade, has now also been isolated by Hesse and Zeitschel from neroli oil, in which it is present in extremely small quantity. They further found traces of acetic and palmitic acids, and a sesquiterpenic alcohol $C_{15}H_{26}O$ (nerolidol) boiling at 276° to 277° . Judging from the low specific gravity of the latter (0,880 at 15°), it appears

¹⁾ Report October 1902, 54.

²⁾ Journal für praktische Chemie II. 66 (1902), 481.

³⁾ Berliner Berichte 26 (1893), 2711.

⁴⁾ Journal für praktische Chemie II. 66 (1902), 484.

⁵⁾ Vol. 67 (1903), 315.

⁶⁾ Berliner Berichte 32 (1899), 2612. — Journal für praktische Chemie II. 66 (1902), 504.

to be an aliphatic compound. The alcohol has a faint odour and is therefore of no importance for the aroma of neroli oil.

On separating¹⁾ the geraniol from the terpineol and linalol, by means of phthalic anhydride according to the process worked out in our laboratory, they obtained a mixture of geraniol and an alcohol isomeric with geraniol, which latter could approximately be separated from the geraniol by treatment with dry calcium chloride, with which, as is well-known, the last-named body forms a solid compound. The alcohol, separated from the solid calcium chloride compound of geraniol by suction, although still considerably contaminated with geraniol, yet differs sufficiently from the latter, so that the assumption appears to be justified, that an alcohol differing from geraniol is present in the constituent which no longer reacts with calcium chloride. In the odour the alcohol greatly resembles geraniol. In the opinion of the authors it has a finer and fresher odour. For the rest, the product (to which the name nerol has been given) differs from geraniol by an "apparently uniform" diphenyl urethane²⁾ melting at 73° to 75° , by the slightly lower boiling point, and by the property of forming no solid compound with calcium chloride.

In addition to the free alcohols geraniol and nerol, their acetic esters geranyl acetate and neryl acetate are, according to Hesse and Zeitschel, also present in neroli oil. Neryl acetate also greatly resembles geranyl acetate in the odour and other properties. With regard to quantity, it is stated that neroli oil contains about 4 per cent. geraniol + nerol, and about the same quantity of the two acetates.

According to our experience (see under petitgrain oil) the statements concerning nerol must for the present be accepted with reserve, as it has not as yet been found possible to separate this body completely from the geraniol, and to identify it with sufficient certainty.

For the aroma of neroli oil, nerol and its acetate have no greater importance than geraniol and its acetic ester, from which in our opinion they do not differ in any very marked degree.

Hesse and Zeitschel have next occupied themselves with the examination of oil of orange-blossom water, and of orange-blossom extract. In the former they detected phenyl acetic acid, phenyl ethyl alcohol, geraniol, and nerol. The oil had the following properties: $d = 0.915$; $\alpha_D = +2^{\circ} 50'$; ester-content 6 per cent.

Owing to the greater solubility of the alcoholic constituents of the orange-blossom and of methyl anthranilate in water, the water-oil contains a comparatively larger amount of these bodies than neroli oil.

¹⁾ K. Stephan, Journ. für pract. Chemie II. 60 (1899), 248.

²⁾ In this connection, compare our observations under petitgrain oil, on page 62.

The essential extract-oil, which can be readily obtained from orange-blossom extract by treatment with alcohol and steam distillation, showed the following constants: $d = 0,913$; $\alpha_D = -2^\circ$; ester-content 41 per cent. calculated on linalyl acetate; content of methyl anthranilate 6,5 per cent. It differs from neroli oil by a much higher ester-content.

We have recently detected in neroli oil, phenyl ethyl alcohol, by its urethane melting at 80° , and we have found that the presence of jasmone is probable, for we obtained from the corresponding fraction a semicarbazone of the melting point 204° to 204° .

Neroli Oil (artificial) "Schimmel & Co." Our original product has reached a very high degree of perfection through the important results of our examinations which we published on pages 52 to 58 of our Report of October 1902, and which we have turned to account in practice. We have made special arrangements for the production of the natural plant-constituents contained in the oil, for which we are very favourably situated.

Our original product should not be confounded with the many inferior mixtures which are much puffed up in the trade and are hawked about at all prices. Where cheapness is a consideration, it is in any case much better to buy a product like ours, and to cheapen it oneself with petit-grain or bergamot oil.

Oil of Nutmeg. Although the light waste material which is used for the manufacture of this oil really forms an article by itself, its price has not been left untouched by the great advance in the price of nutmeg. For a time the demand for the essential oil was exceptionally strong.

Orris Oil. We have received, from a wholly reliable and best informed quarter, the following special report on the present situation of the Florentine market:

The harvest of 1902 gave a total yield of about 1000 tons, or 1 000 000 kilos, since the producers, encouraged by the rising prices in November, also gathered the two-year old roots, and at the same time did not in every locality reduce the new planting to such an extent as at the end of last summer appeared to be the case.

If we add to the above-mentioned crop of	1000 tons
the old stocks still on hand	400 "
we commence with a total quantity of	1400 tons.
Against this, deliveries from the beginning of September to the end of February 1903 amounted to about	470 "
leaving a balance at present of about	930 tons.

But further important quantities have already been sold for gradual forward delivery, and based upon the deliveries which have taken place up to the present, it may be assumed that when the new crop comes in, some 500 or 600 tons may still be available of the above 930 tons. To this must then

be added the result of the coming harvest, which it is as yet impossible to estimate. It may roughly be taken at from 800 to 1000 tons, according as the market-quotations at the harvest-time may induce the producers in a greater or smaller degree to gather the two-years' roots. At the end of November, the prices cif. Hamburg were 40 marks for pickings and 44 marks for assorted roots, and in a few cases higher prices were paid, but with the increasing result of the harvest the speculating mood and gradually also the demand from abroad became more feeble, which reacted adversely on the quotations. As a consequence, the roots can now again be bought:

pickings at 34 to 35 marks cif. Hamburg, and
assorted roots at 36 to 38 marks cif. Hamburg,

not large quantities, but at any rate parcels which impecunious owners now and again put on the market. A further depression in the prices is aimed at from French quarters, although in that case it is hinted pretty clearly, that large parcels would readily be bought at a few marks lower rates for delivery not only in 1903, but also in 1904 and 1905. But naturally nobody here wishes to expose himself for the future at such prices, whilst the already much-suffering producers are least of all desirous of encroaching upon the market at still lower selling prices, though these may possibly have to be conceded later on, whether the growers like it or not, if the foreign buyers remain passive for some time longer. The over-production during the last few years has unfortunately been disastrous to the producers and to all other interested parties, but it is clear that with a gradually diminishing production, normal conditions, and with the latter also normal prices, may once more come back, if not in the immediate future, at least before long.

We have contracted for several hundred tons of the finest natural Florentine roots at the very lowest quotations of the day, and on the strength of these transactions have also sold very important quantities of orris oil. Never before has the perfumery-trade been able to procure this indispensable product at such incredibly low prices, and to use it on such a liberal scale, that violet-preparations can now be produced of unparalleled quality.

In the event of making purchases or placing contracts, the liquid orris oil in tenfold concentration, which we were the first to produce and to place on the market, should be seriously taken into consideration, as, in consequence of decidedly lower manufacturing expenses, it comes cheaper than the concrete oil. Since we introduced it into commerce, it has been used exclusively by a large number of perfumers. It is a matter of special satisfaction to us, that we have created in liquid orris oil a product of the very highest rank, which is of such sterling quality, that it only requires a single trial and calculation in order to recognise at once the advantages which it offers.

As has been the case with every one of the numerous new preparations produced by us in the last few decades, the great majority of our competitors have immediately appropriated also this new creation of ours. We desire to state this here once more, in order to avoid a confusion in the ideas.

We hear that the project of the establishment of a factory for the production of orris oil in the root-growing districts of Tuscany, which we described in our last Report, has up to now not taken any tangible form, owing to the illness of the originator of the idea, Mr. Pegna. When calmly considering the scheme, that gentleman may no doubt arrive at the conclusion that it is not feasible to gather such a large number of root-producers under one flag as would here be the case; and, further, that the cost of production, in spite of the saving in carriage, would be much higher in the case of a factory which produces nothing but the single article orris oil, than with an existing establishment which at the same time manufactures hundreds of other articles.

Patchouli Oil. Since our last Report our supplies of patchouli-leaves have reached us punctually, with the single exception of a parcel of 60 bales per s. s. "Bergedorf", which steamer, as is well known, caught fire when off Messina, and reached Hamburg after great delay. Fortunately the goods had suffered no damage whatever.

According to reports from the Straits Settlements, the article is now most difficult to procure, as it is impossible to obtain the leaves dry during the rainy season. In consequence of this the prices advanced by about 50 per cent., and as it cannot be doubted that the price will remain at this level, the quotations of patchouli oil had to be raised further. For imported oil 50 marks per kilo is already asked. Our product stands in respect of quality above that oil.

We hear from a reliable source that in Java patchouli-plantations have been laid out, from which possibly a crop may be expected before the end of the year. This new source of supply can, under the present conditions, only be welcomed.

Peppermint Oil, American. This important article has passed through a very agitated period. At the time when our last Report was written, there was not the slightest suspicion of the events which subsequently occurred. The value at that time was about \$ 2,— per lb., that is to say fairly normal, and we did not consider it out of the question that with some speculative enterprise it might go slightly higher. We had no idea that at that very time a gang of speculators had already commenced their operations, speculators who were daring enough to buy up 90 per cent. of the existing stocks in order to carry through a corner such as for this article had never been seen before. Within a few weeks the prices were driven up to \$ 5,— per lb., and were maintained at that level for several months.

In view of the results of the harvest and the increased cost of production, nobody would have been surprised to see an advance up to \$ 3,—, but this bewildering state of affairs bore from the first the

stamp of the clumsiest exaggeration, and was naturally opposed by all consumers of peppermint oil. As a consequence business in this article came completely to a standstill. The consumption was restricted to the utmost limits, or else attention was directed to the stocks which were brought to the light at all the principal markets, and which the speculators had not taken into consideration. Moreover France, Italy and Russia placed important quantities on the market and filled many a gap. But the movement received the death-blow when it was found that the bulk of the goods sold by the speculators lacked the properties which good American oil usually possesses. The enormous profit of the corner was not considered sufficient, and it was attempted also to play tricks with the quality. In particular, adulteration with Japanese oil was aimed at; of this oil (as will be found by referring to the statistics on page 61 of this Report) larger quantities than usually were shipped direct from Japan to New York, Philadelphia, San Francisco, Tacoma and Seattle, and heavy purchases were also made in London and Hamburg, with the object of depriving the European market of cheap material. These adulterations were first observed on the English market, but they were also proved by us in quite a large number of samples, and that in oils received from one of the principal speculators who boasts particularly of the "absolute" purity of his oil. Further down we return to this subject. It is only natural that the belief in a continuation of the high prices was greatly shaken by such proceedings. In addition to Japanese oil, erigeron oil is also said to have been used for the adulteration.

Thanks to such preposterous methods, and in the absence of all sympathetic feeling on the part of the European firms chiefly connected with the trade in peppermint oil, the speculators did not succeed in driving the prices up to \$ 6,—, as was the intention. Already in January want of money caused a certain weakness, and offers were made under hand at \$ 4,50.

At present the price is nominally \$ 4,—. Large parcels of the brand H. G. Hotchkiss were recently realised at \$ 3,75 to \$ 3,50.

In London the speculation in peppermint oil has already claimed a victim. A Mincing Lane firm, heavily engaged in this article, has early in March suspended payment.

In the present conditions it is in the highest interest of every consumer to cover only the most necessary requirements. We have reduced the prices of our two brands **FB** and **FS & Co.** by 4/- per lb.

As already mentioned, the rise in the prices of American peppermint oil has amongst others also led to extensive adulteration. In our laboratory numerous samples were examined which showed pronounced differences in specific gravity and optical properties from the

normal distillate, but which above all attracted attention by their difficult solubility. It is a matter of course that these oils also showed a very low menthol-content. We mention below a few oils which had been adulterated to a specially large extent, in order to show the impudence with which these adulterations are carried out: —

	d_{15}°	a_D	Total alcohol %	Solubility
1	0,8888	—15°40'	33,8	} Insoluble in 10 volumes 70 per cent. alcohol.
2	0,8886	—17°24'	35,2	
3	0,937	—12°44'	45,9	
4	0,8867	—9°41'	26,1	

What has been said above applies particularly to the last-mentioned oil, which, contrary to the other three oils, only formed a cloudy solution even in 15 to 20 volumes absolute alcohol. A more detailed examination showed in this case an addition of about 60 per cent. mineral oil, an adulteration which must be characterised as unheard of.

The same observations have been made by Parry who, in "The Chemist and Druggist"¹⁾, publishes the examination of a number of American peppermint oils which show entirely similar deviations from normal oil as the examples mentioned by us. He states that he has lately had before him more adulterated oils than pure ones.

On a previous occasion Parry had already pointed out a case of adulteration of peppermint oil with light oil of camphor²⁾. Such oils are characterised by exceptional insolubility and low menthol-content, and especially by the fact that the fractions obtained on distillation below 200° to 205°, are much larger than in the case of pure peppermint oil.

Peppermint Oil, Italian. In our Report of October 1902 we gave on page 66 particulars of Italian peppermint oil. A few peppermint oils also originating from Piemont have been examined by C. Ed. Zay³⁾; we reproduce below in tabulated form (I to III) the actual results obtained by the author, and add for purposes of comparison the values which we have since obtained in examining some other samples of the same origin (IV to VI).

¹⁾ Vol. 61 (1902), 948.

²⁾ The Chemist and Druggist 61 (1902), 520.

³⁾ Staz. sperim. agrar. ital. 35, 816; according to Chem. Centralblatt 1903, I, 331.

	$d_{15^{\circ}}$	$\alpha_{D16^{\circ}}$	$n_{D16^{\circ}}$	Total menthol	Ester-menthol	Free menthol
I.	0,916	— $2^{\circ} 34'$	1,468	55,5 %	9,72%	45,78%
II.	0,9171	— $10^{\circ} 41'$	1,467	58,6 "	7,10 "	51,5 "
III.	0,9256	— $7^{\circ} 4'$	1,468	45,0 "	6,01 "	38,99 "
IV.	0,9122	— $16^{\circ} 21'$	1,46733 (20°)	52,5 "	7,89 "	44,61 "
V.	0,916	— $13^{\circ} 17'$	1,46783 (20°)	53,07 "	9,66 "	43,41 "
VI.	0,9157	— $12^{\circ} 34'$	1,46783 (20°)	50,95 "	9,87 "	41,08 "

The oils IV to VI examined by us did not form a completely clear solution with 70 per cent. alcohol, and the solutions in 80 per cent. alcohol which were at first clear, became cloudy when more solvent was added.

We wish to avail ourselves of this opportunity to correct a slight error which has crept in the previous article. It is mentioned there, that the menthone-content of the sample amounted to 23 per cent.; in reality it only amounts to 8,16 per cent., and this result agrees very well with a further examination which was subsequently made with another sample. The mistake was, that the difference in the saponification numbers of the acetylated oil before and after the conversion of menthone into menthol, was given as the menthone-content.

Peppermint Oil, Japanese. According to information from our friends in Japan, dating from the end of October last year, the result of the last harvest is as follows: —

Bingo Bitchin	1 st crop	4 000 cattiees.
"	" 2 nd	" 30 000 "
"	" 3 rd	" 26 000 "
Yonezawa	1 st	" 25 000 "
"	2 nd	" 15 000 "

Total 100 000 cattiees

or about 60 000 kilos,

against 80 000 cattiees, or about 50 000 kilos, in 1901. It was therefore fairly normal, and sufficient for the demand.

If, in spite of this, the value of the article is exceptionally high, the fault lies solely and exclusively with America, for the purchases on American account were made in such haste, that the Japanese soon discovered what the object was of these transactions.

Our cheapest purchase was in July last year at 3/3; since then the rise occurred as follows: —

Cheapest quotation in July	1902, about	3/3 per lb.
Average	" " August	" " 4/4 " "
"	" " September,	" " 5/- " "
"	" " October	" " 5/- " "
"	" " November,	" " 7/6 " "
"	" " December,	" " 8/6 " "
"	" " January 1903,	" " 13/- " "

With the January quotation the highest price was reached. The prices then remained at the same level, and when in February and March several large parcels were sold by auction in London and fetched prices between 8/- and 9/-, the tendency became less firm, and the prices since then are nominal.

We are convinced that the fall in the quotation of Japanese oil will go hand in hand with that of American oil, the same as was the case with the rise. On the supposition that this argument is correct, it is at present advisable to exercise caution in purchasing.

The shipments of liquid Japanese oil since 1st August last year were as follows: —

to Hongkong	7097 cattiees
„ London	2700 „
„ Hamburg	2700 „
„ Havre	2475 „
„ New York	1350 „
„ San Francisco . . .	1125 „
„ Philadelphia	900 „

The comparatively large shipments to Hongkong would probably be bound chiefly for Hamburg and London, as our direct importation during that time is decidedly larger than the figures given for Hamburg.

Peppermint Oil, Mitcham. In the better qualities there is a total absence of offers, and it would be a difficult matter to hunt up parcels of any importance in England. With the enormous prices of American oil, there is a very brisk demand for English oil. In spite of the notorious lack of pure original distillates, "Mitcham" oil is hawked about at all prices, down to 52 marks per kilo, prices which can only raise a smile on the face of those who are behind the scenes.

Experiments made by E. Charabot and A. Hébert¹⁾ have shown that mineral salts which have been applied to the soil in the neighbourhood of a plant, effect a reduction in the water-content of the latter. The experiments were made with the peppermint plant, which was submitted to the action of common salt, calcium chloride, sal ammoniac; the sulphates of sodium, potassium, ammonium, iron, and manganese; the nitrates of sodium, potassium, and ammonium; and di-sodium phosphate. The most powerful action is exerted by nitrates, especially sodium nitrate; the least powerful by di-sodium phosphate.

¹⁾ Compt. rend. 136 (1903), 160.

Petitgrain Oil. In November last year the report was circulated, that negotiations were being carried on between the distillers in Paraguay for the formation of a "ring", in order to monopolise the production, and as a consequence a prospect was held out of higher prices. But as we learn from a reliable source, this syndicate has not succeeded on account of the opposition from one of the oldest and most important producers, and the situation will therefore practically remain as before. The export of petitgrain oil from Paraguay amounted in 1901 to 17 044 kilos, value 25 566 gold pesos (1 peso = 4 s.). The quantity as given may agree with the facts, but the value is placed much too low, which shows once more that statistical figures have only a comparative value.

It might be assumed that the geraniol-like alcohol, designated by Hesse and Zeitschel as nerol, also occurs in petitgrain oil which is closely related to neroli oil. von Soden and Zeitschel¹⁾ have meanwhile produced from saponified petitgrain oil, by treatment with phthalic anhydride and calcium chloride, a fraction which had the properties mentioned by Hesse and Zeitschel. It is stated that petitgrain oil contains about 2 per cent. of this body. The boiling point of the preparation which in the opinion of the authors is now only contaminated with about 10 to 15 per cent. geraniol, is given by them as 225° to 227°, at atmospheric pressure; $n_D = 1.480$, $d = 0.880$. The odour is said to be decidedly fresher than that of geraniol. The compound absorbs 4 atoms bromine. Boiled with acetic anhydride, it yields quantitatively an ester having an odour resembling that of geranyl acetate. The boiling point of the ester at 25 mm is 134°; $d = 0.917$.

The formate is formed in the cold when a mixture is made with concentrated formic acid; it has an odour like geranyl formate. Boiling point 119° to 121°, at 25 mm; $d = 0.928$.

These compounds are naturally not uniform bodies, but contaminated with the corresponding esters of geraniol. It is suspected that nerol, along with geraniol, is present in most oils which contain the last-named body. von Soden and Zeitschel do not state on what grounds they assume that the admixture of geraniol in the preparation produced by them amounts to only 10 to 15 per cent.

As we have also occupied ourselves since some time with the examination of petitgrain oil (see our Report of October 1902, page 68) we have, in isolating the alcohols which are present in this oil, also directed our attention particularly to the separation of a compound having the properties of nerol, from the geraniol fraction of this oil.

¹⁾ Berliner Berichte 36 (1903), 265.

We are in a position to confirm von Soden and Zeitschel's statement that here also, after removing the terpineol and linalol by means of phthalic anhydride, a mixture of alcohols remains, which unites only partially with calcium chloride. The product which we purified by treating it twice with calcium chloride, showed a boiling point a little lower than geraniol.

The principal fraction boiled under atmospheric pressure at 225° to 227° , or from 106° to $107,5^{\circ}$ at 7 to 8 mm; the following fraction from 227° to 228° at atmospheric pressure, or from $107,5^{\circ}$ to 109° at 7 to 8 mm.

The odour of these fractions very much resembles that of geraniol, but differs from that of citronellol. The diphenyl urethane was produced with 4 g of the principal fraction. We readily obtained a solid product which after being recrystallised once from dilute alcohol, melted indistinctly at from 60° to 64° . The melting point could not be raised in any marked degree (65° to 66°), in spite of repeated recrystallisation from alcohol. Only by partly dissolving the preparation in cold petroleum ether, and allowing the solvent to evaporate, we were able to obtain crystals which showed the melting point 73° to 75° , indicated by Hesse and Zeitschel for neryl diphenyl urethane. The melting point of this product was, however, after further recrystallisation from petroleum ether, raised to 80° to 81° , i. e. the melting point of geranyl diphenyl urethane.

It remains, therefore, open to doubt, whether the melting point given by Hesse and Zeitschel for neryl diphenyl urethane, is correct.

We will now compare the physical constants of the 'nerol' produced by us (which essentially agree with the figures given by v. Soden and Zeitschel), with the constants of the pure geraniol regenerated from the solid calcium chloride compound:

Nerol	Geraniol
Boiling point 225° to 227°	Boiling point 229° to 230°
$d = 0,8804$	$d = 0,880 - 0,883$
$\alpha_D = + 0^{\circ} 17'$	$\alpha_D = \pm 0^{\circ}$
$n_{D17^{\circ}} = 1,47665$	$n_{D17^{\circ}} = 1,47660$

It will be seen that the differences are so small, that on the ground of a determination of the constants, a differentiation of the compounds is not possible. For this reason it requires several further examinations to establish whether nerol, according to its principal quantity, represents a new alcohol differing from geraniol.

As the nerol produced according to Hesse, v. Soden and Zeitschel is still strongly contaminated with geraniol, we have attempted by another method to purify it further from geraniol.

When geraniol is heated with concentrated formic acid at 80° to 100° , it decomposes, like linalol, almost quantitatively into terpenes and polyterpenes, with loss of water. It might be possible that nerol would be less readily attacked by formic acid, and that, therefore, by heating crude nerol with formic acid, nerol might be produced free from geraniol by means of phthalic anhydride from the saponified mixture of terpenes, polyterpenes, and neryl formate. We accordingly heated 7 grams of the crude nerol (fraction 225° to 227°) obtained by Hesse and Zeitschel's method, with 10 grams concentrated formic acid on a water bath, until the turbidity due to loss of water occurred, and thereupon immediately diluted with water. The quantitative saponification of the washed neutral oil showed that it contained 39 per cent. of a formate, calculated on neryl formate. The bulk of the washed mixture, consisting of terpenes, polyterpenes and the unattacked alcohol, distilled at 15 mm from 80° to 170° . This fraction which still possessed a rose-like odour, was, after adding a small quantity of benzene, with the same weight of phthalic anhydride heated on a water bath, and the acid phthalic ester of the alcohol thereby formed extracted with soda, and all impurities removed by extraction with ether. When the phthalate was heated with soda liquor, an alcohol with a geraniol-like odour was separated, which was obtained by steam-distillation. The quantity was too small to determine whether this alcohol differs from geraniol.

We do not doubt, however, that v. Soden and Zeitschel will soon succeed in producing nerol quite free from geraniol, and in elucidating the nature of this compound which resembles geraniol in such an extraordinary degree.

Pine-needle Oils. Of these products, the distillate from *Pinus Pumilio* still plays the most important part; this is now so much in demand, that we had the greatest difficulty in obtaining the necessary supplies. The project, previously mentioned by us, of taking up the distillation on the slopes of the Carpathian Mountains in Hungary, has not yet been realised. The present moment would be favourable for the introduction of a new kind.

The consumption of the fine Siberian pine-needle oil which is absolutely pure and at the same time extremely moderate in price, has developed enormously. Last year it was already used by us in quantities of thousands of kilos. The Swiss distillers already demand higher prices for the extra-fine quality distilled from the cones of *Abies pectinata*. The exquisitely fine oil from *Abies alba* takes, as regards quality, now as before the first rank, and it sells so rapidly that we are never able to accumulate a stock of it.

Rose Oil, Turkish. The prices of the better-class brands have on the whole remained unchanged. The purchase-prices of these

brands amount to about 600 marks per kilo, whilst ordinary commercial oil can be bought at all prices. Nothing can as yet be said of the new harvest. The winter in Roumelia was very mild, and the rose-bushes do not appear to have suffered.

By far the most important question for the rose-oil trade which at present claims attention, is the position of the Bulgarian Government towards the adulteration-problem, a question which has already been discussed so often in our Reports, and which up to now, for the most diverse reasons, has not yet been solved.

On the initiative of some deputies, there has been deposited at the Bureau of the National Assembly a new project of a law which is to guarantee the purity of rose oil. According to this project every admixture to rose oil, of whatever nature, is prohibited under penalties, and that not only during distillation, but also during the sale. The distillation is to be carried out in common establishments under control of a Government official; the produced oil is stored in special premises connected with the Agricultural Offices. Every producer receives from the particular Office a voucher giving the quantity, solidifying point, name of the distillation and origin of the roses, and on the strength of such voucher the producers will be able to obtain advances on their oil from the Loan Offices, or they can sell the oil to merchants against delivery of the voucher. Every purchaser can on presenting the voucher demand delivery of the oil mentioned in it. Moreover, the "Caisse Agricole" gives to the purchaser a sealed note which has been endorsed by a notary, on which the quantity purchased and exported is stated. Every consignment which is exported is accompanied by a certificate mentioning the name of the exporter, the place of origin, the guarantee of purity, and the solidifying point.

These certificates are returned by the sender within 6 months to the particular office, after having been signed by the purchaser and his signature legalised.

We are, however, informed that the Government as well as all interested parties are opposed to this project. It is the work of people who have no thorough knowledge of the article, and who do not know that it would be impossible to carry out such a law in practice, and that it would consequently be useless.

With regard to the matter of the Government-seal to coppers, to which we referred last year, a commencement has now been made to provide rose oil with such seal. The coppers have also a label attached with the following inscription: Douane Plovdive - Bulgare, Provenance Bulgare, S. G. D. G. (sans garantie du gouvernement). A tax of 30 centimes is levied for the seal and label.

The utility of these measures is inexplicable to anyone who has a practical insight into the conditions, for the insignia are

attached to every copper, no matter whether it contains pure or adulterated oil.

It follows from the foregoing that the question of submitting rose oil to official control, which at the time was introduced with great emphasis, remains unsolved just as before.

According to the particulars recently published by the Statistical Office, the total export of rose oil from Bulgaria amounted in 1902 to 3676 kilos, value 2609159 francs, against 3027 kilos, value 2140538 francs, in 1901. The exports of 1902 therefore exceed those of the preceding year by 649 kilos, and 468621 francs. In the month of December 1902 the exports of rose oil came to 227 kilos, value 151817 francs, of which to Austria-Hungary 5 kilos, value 3425 francs, to the United Kingdom 22 kilos, value 15154 francs, to Germany 29 kilos, value 19753 francs, to Turkey 6 kilos, value 3661 francs, and to France 145 kilos, value 96132 francs.

Rosemary Oil, Dalmatian. In view of the high prices and the scarcity of the French distillate, an exceptionally strong demand exists for Dalmatian oil, which has led to a slight increase in the prices. The adulterated qualities which are met with in commerce in large quantities are not affected by the present state of affairs.

As is well known, the distillation of rosemary oil is carried on on the Dalmatian island of Lesina. In our Report of October 1896 we gave a detailed description on the subject, based on personal observations. In the meantime, the situation has undergone a decided change. The distillation is still carried on in the two villages Bruschje and Grablje, which from time immemorial have been the seat of the production; the process was formerly very primitive and took up much time. At the instigation of the Governor of Dalmatia, two limited companies have now been formed for the production of rosemary oil, which work with German steam-distilling apparatus of the most modern construction, and are said to supply an excellent article. It is stated that the peasants are quite enchanted with these installations, and are vying with each other in their work. With the old, difficult manufacturing process, the two villages had an annual revenue of about £ 900,— from rosemary oil, whilst in the present season, with much less work, they have already received about £ 1200,—. The distillation of sage, which plant grows there in enormous quantities, has also succeeded excellently, and a remunerative trade in oil of sage¹⁾ is also anticipated.

It is a pleasure to find that civilisation is gradually penetrating even into remote districts with prosperity following in its train.

¹⁾ "Gartenflora", Zeitschrift für Garten- und Blumenkunde 1903, Vol. 4.

Rosemary Oil, French. The final result of the distillation in the South of France has fallen below the most modest expectations. The acquisition of larger parcels of pure oil is a matter of the greatest difficulty.

Oil of Rue. From the work of Mannich¹⁾ on the ketones of oil of rue, which has been published again in connected form, we make some abstracts as an addition to what we mentioned on the subject in our last Report²⁾. The ketone $C_{22}H_{42}O$, obtained from methyl nonyl ketone in a manner analogous to the condensation of acetone with hydrochloric acid gas, can again be converted into the original ketone by means of 60 per cent. sulphuric acid. The picrate of its amido-guanidine compound melts at 125° to 126° . The methyl heptyl ketone is capable of analogous condensation. The ketone $C_{18}H_{34}O$ thereby formed, boils at 184° to 187° (14 mm), its amido-guanidine derivative has the melting point 130° to 131° .

A German oil of rue recently examined by J. Houben³⁾ had the melting point $9,3^{\circ}$, and showed a striking blue fluorescence, which was caused by a compound which could be abstracted from the oil by shaking with dilute sulphuric acid. Owing to the smallness of the quantity of oil which was obtained from the sulphate solution on neutralising the latter, the author was unable to make a further examination of the compound. In this connection we would point out that the same body was discovered by us already some time ago in German oil of rue, and that, according to our observations, it may most probably be identic with methyl ester of methyl anthranilic acid. We would refer to our communication in the October Report of 1901, page 46.

In addition to a small quantity of an acid distilling at 236° to 238° , which was probably caprylic acid, and another small quantity of a phenol-like body of the melting point 156° , Houben isolated from 500 grams oil 355 grams methyl nonyl ketone and 12 grams methyl heptyl ketone. According to his statements, the latter boils, contrary to what Thoms has stated⁴⁾, at 194° to 196° (80° to 82° at 15 mm). The boiling point of methyl nonyl ketone was found at 228° to 230° , at 18 mm pressure at 118° . Thoms gives it as 223° to 224° , v. Soden⁵⁾ and Henle as 230° to 231° . Methyl nonyl ketone has the following constants: specific gravity 0,8295; solidifying point $+13^{\circ}$.

¹⁾ Berichte der deutsch. pharm. Ges. **12** (1902), 267.

²⁾ October **1902**, 76.

³⁾ Berliner Berichte **35** (1902), 3587.

⁴⁾ Report April **1901**, 52.

⁵⁾ Report October **1901**, 47.

The pure ketone shows no fluorescence. The fluorescent ketone described by Charabot-Dupont-Pillet¹⁾, was clearly contaminated with the above-mentioned basic constituent.

The methyl heptyl carbinol obtained from methyl heptyl ketone by reduction with sodium in an aqueous-etheral solution, — a body which from another side has recently been detected in oil of rue (see below) — is a liquid with a pleasant odour, boiling at 193° to 194° (90° to 91° at 12 mm). Dimethyl heptyl carbinol produced from the ketone by Grignard's reaction with methyl magnesium iodide, boils at 96° to 98° (13,5 mm). The carbinol boils at 10 mm pressure at 115°, at 14 mm at 120°; its acetic ester distils at 122° (11 mm). The second reduction-product from methyl nonyl ketone, representing 10 to 15 per cent., is methyl nonyl carbinol pinacone, a solid body of the boiling point 215° (10 mm). Dimethyl nonyl carbinol boils at 117° to 118° (12,5 mm). According to Houben's statements, the conversion of the methyl nonyl ketoxime (after Beckmann) with concentrated sulphuric acid, does not take place in accordance with the observations made by Hantzsch²⁾ with ketoximes; for the author found, contrary to Thoms³⁾, in addition to acetyl nonyl amine, also a large proportion of capric acid amide.

F. B. Power and H. Lees⁴⁾ also report on a number of interesting bodies detected in oil of rue. The origin of the material examined could not be determined with certainty, but the authors believe, on the strength of the resemblance of its chemical and physical constants to those of the oil examined by von Soden and Henle⁵⁾, that it was an Algerian rue oil. It had a bright-yellow colour without fluorescence, the specific gravity $d_{\frac{15.5}{16}}^{15.5}$ 0,8405, the optical rotation $\alpha_D - 3^\circ 48'$, and was soluble in 2 parts 70 per cent. alcohol. The quantity of oil used was 1800 grams. By shaking with 20 per cent. sulphuric acid, a basic body was abstracted from the oil, but this body (contrary to the base of rue oil discovered in our laboratory) showed no blue fluorescence, and had an odour reminding of quinoline. The crystals of the melting point 156°, previously found by Thoms⁶⁾ and lately also by Houben in the German oil, were proved by Power and Lees to be salicylic acid, clearly originating from its methyl ester which was obtained in small quantity along with it. The properties of the two ketones which are also present in this oil are as follows:

¹⁾ Les huiles essentielles, p. 283.

²⁾ Berliner Berichte **24** (1891), 4021.

³⁾ Berichte d. deutsch. pharm. Ges. **11** (1901), 3.

⁴⁾ Journ. chem. Soc. **81** (1902), 1585.

⁵⁾ Pharm. Ztg. **46** (1901), 277 and 1026. — Report October 1901, 47.

⁶⁾ loc. cit.

Methyl heptyl ketone:

Boiling point $194,5^{\circ}$ to $195,5^{\circ}$
(763 mm).

Specific gravity d_{16}^{14} 0,8296.

Melting point of the semicarbazone
 119° to 120° .

Methyl nonyl ketone:

Boiling point 229° to 233° (759 mm),

„ of the ketone regenerated
from the semicarbazone $231,5^{\circ}$
to $232,5^{\circ}$ (761 mm).

Specific gravity $d_{16}^{20,5}$ 0,8263.

Melting point of the semicarbazone
 122° .

Valeric acid, present in the oil perhaps as ethyl ester, was found on saponification of a fraction boiling from 165° to 170° . 1-Pinene was contained in the portions of the same boiling point, limonene and cineol in the fractions boiling from 170° to 185° . The presence of this hydrocarbon was proved by the nitrosochloride and the latter's nitrol piperidide. The two last-named bodies could be identified by the tetrabromide (m. p. 103°) and the iodol derivative (m. p. 114° to 115°) respectively, and by the hydrobromide of cineol (m. p. 55° to 56°). From the saponification liquors of the fractions boiling above 185° , an acid was obtained which distilled below 120° , and which was recognised as acetic acid by the analysis of its silver salt. Special interest is also attached to the presence of methyl heptyl and methyl nonyl carbinols in oil of rue, the secondary alcohols produced by Mannich and by Houben from the corresponding ketones. The authors succeeded in detecting the bodies in the fractions of the boiling points 190° to 200° and 210° to 235° respectively. The physical constants of the compounds are as follows:

Methyl heptyl carbinol:

Boiling point 195° to 196° .

„ of the carbinol purified by
the acetyl compound 198° to
 200° (765 mm).

Specific gravity d_{16}^{19} 0,8273

Optical rotation α_D — $3^{\circ} 44'$
(50 mm).

Methyl nonyl carbinol:

(obtained from the acetyl compound of
the crude carbinol)

Boiling point 231° to 233° .

Optical rotation α_D — $1^{\circ} 18'$
(25 mm).

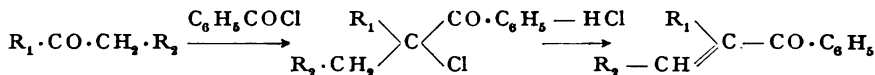
The corresponding acetates boil at 213° to 215° and 245° respectively.

Elementary analysis, and the formation of the ketones of the corresponding boiling points on oxidation of the carbinols with chromic acid, prove that the two products may be considered as methyl heptyl carbinol and methyl nonyl carbinol.

The oil passing over between 250° and 320° has a blue colour and a herb-like odour. The ketone content, according to the authors, amounts to 80 per cent., the content of alcohols to about 10 per cent.

The ketones are present in about equal proportion. The presence of terpenes (pinene, limonene) leads to the suspicion that the oil examined was adulterated.

Power and Lees had at first attempted to separate the ketones of rue oil from the alcohols by treatment with benzoyl chloride, in the expectation that they would subsequently be able to obtain the high-boiling benzoic esters of the alcohols by fractionating. But, as Lees¹⁾ states in a later work, this method proved unsuitable, as the ketones also yielded high-boiling condensation products with benzoyl chloride, which on further examination were recognised as the benzoic esters of olefinic alcohols. Their formation may be explained by the following formula:



The compounds correspond to the enol-form of acidyl aceto-acetates produced by Claisen and Haase²⁾. On hydrolysis they are reconverted into the original ketones with intermediate formation of homologous vinyl alcohols.

In the course of an examination of oil of rue carried out with Power, Lees³⁾ produced from secondary hexyl aceto-acetic ether, by splitting off the ketone, methyl β -methyl hexyl ketone, which was obtained in a yield of 80 per cent. in the form of a pleasant smelling oil of the boiling point 184° at 769 mm, and the specific gravity (d_{16}^{15}) 0.8319. Its oxime is liquid; the semicarbazone shows the melting point 75° .

Oil of Muscatel Sage, which is characterised by an odour approaching that of ambergris, has lately been purchased in large quantities, which cannot be replaced until the late autumn. We have only a few ounces at disposal.

Sandalwood Oil, East Indian. With regard to the disease which has broken out in some districts among the sandalwood plantations, and which we first mentioned in our Report of October last year, there is now published in number 1 of "The Indian Forester" (January 1903) a very detailed report from the Government botanist, C. A. Barber of Madras, who has inspected these districts by order of the Government. We reproduce below the most essential points of this report: —

The disease, called "spike", appears to be of recent occurrence; it is believed that the first traces have shown themselves 4 to 5 years ago. Since that time whole tracts have been cleared by it, especially in localities where

¹⁾ Journ. chem. Soc. **83** (1903), 145.

²⁾ Berliner Berichte **33** (1900), 1242.

³⁾ Journ. chem. Soc. **81** (1902), 1594.

the trees grow close together. It is assumed that the disease is infectious, although no strict proofs hereof exist. The disease manifests itself in this manner: the young shoots and leaves, instead of having the beautiful appearance of their kind, commence to grow out stiff and straight. The leaves stand erect like bristles. In the course of the disease the leaves become constantly narrower and more pointed, and from year to year fewer, until they have the appearance of fine ears with 4 rows of bristles. Then the tree soon dies. From all reports it appears that the course of the disease is very rapid, mostly extending only over a few months. The disease does not, as was at first believed, attack only the roots, but the whole plant. No doubt it begins at the roots whose extremities gradually die off, by which the supply of water and salts is cut off. The abnormal conditions which then occur in the formation of the blossoms, must bring about the destruction of the tree. For this reason, the further study of the still unexplained cause of the disease must be directed to the extremities of the roots.

In the same number of the above-mentioned periodical Sir Dietrich Brandis expresses himself on the "Treatment of the Sandal-tree". He suggests the careful study of those plants which appear as "companions" of the sandal-tree. He further recommends a close undergrowth in the sandalwood-plantations. The cultivation should be carried on with self-propagated seedlings, and a sufficient area should be reserved, where the trees, protected from fire and contagion, can develop further in an undisturbed manner. The distances between the plants should be sufficiently large to allow of the free development of the crown of the tree.

It is clear from the foregoing that the British Government is thoroughly following up the evil, and with the help of the capable botanists whom it has in its service, will find ways and means to remove it before it spreads to the other districts. If, against expectation, the disease should extend over all sandalwood districts, the market would, for the time being, receive very large supplies of wood material (as the dead trees represent normal material); but when this is used up, a calamity could scarcely be avoided, until the aftergrowth has advanced far enough to supply a substitute.

The prices of sandalwood oil, through a competition which is constantly increasing in numbers and intensity, have been depressed to a level which is out of all proportion to the cost of production and trouble. Although we take no part in the price-cutting we are unable to accumulate stock, a proof that a reliable and strictly first-quality oil is still appreciated.

The „Oranje", manufacturers of essential oils at Amsterdam, have issued a circular dated January 22nd 1903, in which they pretend to be particularly well placed for the distillation of Sandalwood oil, owing to contracts with the Mysore Government for the purchase of the wood. As we had reason to believe that this statement was not in

accordance with the facts, but merely made for the purpose of “advertising” the firm’s importance, we applied direct to the respective officials at Mysore, from whom we promptly received the following reply, which in point of clearness leaves nothing to be desired: —

(General Serial No. 30.)

1903.

From

M. Muttannah, Esquire, R. B.,
offg. Conservator of Forests in Mysore,
Bangalore.

To

Messrs. Schimmel & Co.,
Miltitz, Leipzig,
via Brindisi.

Dated } 23rd March 1903.
Despatched } Camp Arsikere.

Received

Camp No. 622

No.

} 1903.

Enclosures Number.

Sir,

With reference to your letter of the 30th January last, addressed to Mr. J. L. Pigot, late Conservator of Forests in Mysore, I have the honour to inform you that Mysore Sandalwood is always sold by auction, and no contracts exist with any firm or person for the private sale of Sandalwood. The statement published by the “Oranje”, that they have important contracts with the Mysore Government, is therefore not true. I accordingly request you to contradict this statement and to give wide publicity to the fact. Thanking you for the information you have been good enough to furnish in the interest of Sandalwood trade,

I have the honour to be,

Sir,

Your most obedient servant,

M. Muttannah,
Offg. Conservator of Forests
in Mysore.

This document needs no further illustration: it shows, what kind of doubtful means are often employed to mislead buyers.

Sandalwood Oil, West Indian. The distillation-waters of West Indian sandalwood oil also yield on cohobation a yellow-coloured first fraction containing alcohol, in which methyl alcohol, diacetyl and furfural could be detected in the manner repeatedly described.

Savin Oil. On a previous occasion¹⁾ we have already mentioned that the first runnings of savin oil contain diacetyl; methyl alcohol, and furfural, bodies which usually occur along with this compound, could at that time, however, not be detected.

We have now been able to isolate all these three compounds, in considerable quantities, from the cohobation waters of savin oil. The identification took place in the usual manner.

Spearmint Oil. At the present time America controls the market of this oil completely, as for many years there has been no question of a German production. The prices, which have risen about 100 per cent., must be paid, whether one likes it or not. For the rest, everything depends on the result of the distillation in the coming autumn.

Spike Oil. This oil is in the same position as oils of lavender and rosemary, but with this difference, that here the advance in the prices is about half-way between the other two. As our buyer called our attention in good time to the critical situation, we were able to secure large parcels before the rise asserted itself to its full extent; and we are now in a position to supply our clients in an excellent manner. The stocks in the hands of producers are practically exhausted.

Star-anise Oil. Since the date of our last Report, efforts have repeatedly been made in China to drive up the prices, but these have met with no response. In fact, it cannot have escaped the attentive observer, that since several years the speculative spirit for such like articles has disappeared, a spirit which in previous years asserted itself at every opportunity, especially on the London and New York markets. A year seldom passed by without more or less important fluctuations in the prices of Chinese oils. The cause of this disinclination may possibly be this, that the production of star-anise oil has increased, but the consumption has declined owing to the competition of anethol.

The Chinese exports cannot be ascertained, as the statistics give star-anise oil not by itself, but jointly with cassia oil.

The shipments from Tonquin in 1902 were:

1050 cases ex Pakhoi
620 „ „ Haiphong
<hr/> Total 1670 cases of 30 kilos each.

¹⁾ Report October 1900, 62.

According to reports from Tonquin, the prospects of this year's harvest are exceptionally favourable. The crop is estimated at double that of 1902.

Oil of Tansy. The American distillate which in point of quality is entirely reliable, has been carried along with the general upward movement of essential oils of American origin, and has been driven up to almost the double value.

Under these conditions it will be more advantageous to distil this oil here in the coming summer.

Thyme Oil. According to a commercial Report issued by the British Board of Trade¹⁾, it would appear that the manufacture of essential oils in the island of Cyprus is extending more and more. Since some time the manufacture of red thyme oil (which to all appearances is obtained from an *Origanum* species), marjoram oil and rose oil has received special attention, and for these Cyprus seems to offer a large field. For example, the export of red thyme oil amounted in 1899/1900 to 237 lbs., in 1901/01, to 615 lbs., and in 1901/02 to 1086 lbs. The price for the former in England was 3/- per lb., which seems a very fair one considering that pure oil of thyme is sold for at least 5/- per lb. *Origanum* is to be found at present growing wild only, chiefly in the forests, but the quantity growing there is so important, that a much greater quantity of oil could be produced than that distilled last year. Rose oil is at present only produced on a small scale, but this branch of manufacture appears to be also growing. For instance, large plantations of *Rosa damascena* were made last year in the neighbourhood of Milikouri and Pedoula, the centre of the rose-oil and rose-water manufacture.

Tuberose Oil. Since A. Verley²⁾, four years ago, published his communication on the oil of tuberose-blossoms, this oil has not again been submitted to an examination. Verley had isolated from the essential oil of tuberose about 10 per cent. of a compound which he calls tuberone. Nothing definite has become known of the properties of this body, which appears to be a ketone, and is said to be composed according to the formula $C_{13}H_{20}O$. Even less is known of the remaining constituents of this oil. In connection with our other chemical examinations of the blossom-oils which are so important for the better-class perfumery, we have also occupied ourselves with tuberose oil. A result of the work which is not yet concluded may be communicated in this place.

The crude material employed for the examination was extract of tuberose-blossoms, as an essential tuberose-oil is not on the market.

¹⁾ The Chemist and Druggist **61** (1902), 1026.

²⁾ Bull. Soc. chim. III. **21** (1899), 307.

Extract of tuberose-blossoms is a brown salve-like mass, which, like all pure blossom-extracts, consists chiefly of wax and paraffin-like substances which have no value for the odour.

In order to obtain from this the essential oil, 100 g extract were distilled out with water vapour, whereby a milky, turbid, watery distillate was obtained. The essential oil extracted with ether from this distillate after addition of common salt, had the characteristic odour of the tuberose, and showed a distinct blue fluorescence. The latter points to the presence of methyl anthranilate which has repeatedly been detected in flower-oils. The yield of oil only amounted to 5 g, but in any case the extract contains more — perhaps double that quantity — for it is a difficult matter to distil the oil out until all odour has disappeared. At 5 mm pressure the oil distilled from 60° to 140°. With the fraction boiling about 140°, which amounted to over 1 g, and in which tuberone must be present, it was attempted to produce an oxime. After boiling with alcoholic potassa and hydroxylamine hydrochloride, the odour of the fraction had undergone no change. A solid compound could not be separated from the reaction-product. The remaining 4 g oil were oxidised with dilute solution of potassium permanganate, with the application of heat. The oxidation which at first progressed rapidly, became gradually slower, and there remained at last an oil which was oxidised with difficulty, and whose odour reminded of methyl benzoate. This oil, which was fairly volatile with water-vapour, was distilled off in a current of steam. It was heavier than water, but its quantity was too small to allow of an exact determination of the constants. That this oil actually consisted chiefly of methyl benzoate, was shown when it was heated with alcoholic potassa, when a good yield of benzoic acid was obtained. The melting point of the separated recrystallised acid lay at 122°.

The silver salt of this acid contained a quantity of silver calculated for silver benzoate.

0,0956 g yielded 0,0451 g = 47,17 per cent. Ag.

Calculated for C_6H_5COOAg = 47,16 " " "

As methyl benzoate is only difficultly attacked by dilute 3 to 4 per cent. solution of potassium permanganate, even when boiled, the method described is suitable for the separation of this compound in oil of tuberose, and occasionally also in other essential oils¹⁾.

When sulphuric acid was added to the oxidation liquor, an acid of a fatty consistency separated out, which has not yet been submitted to examination. After prolonged standing there sublimed from the mass crystals which melted at 120°, apparently benzoic acid.

¹⁾ Compare Oil of Cloves

Verbena Oil. An examination of verbena oil from Grasse has been published by E. Theulier¹⁾. The oil, obtained in a yield of 0,072 per cent. from the fresh leaves of *Verbena triphylla*, had a bright yellow colour, reminded in the odour somewhat of lemongrass oil, and showed the following constants: $d_{15} = 0,919$; $n_D = 1,620'$; ester-content (calculated on linalyl acetate) 11,20 per cent. The oil was insoluble in 80 per cent. alcohol, but dissolved in an equal volume of 90 per cent. alcohol, and when more of this solvent was added, small white crystals separated out. The same body separated out when the oil was cooled in a freezing mixture; after repeated recrystallisation from strong alcohol it melted at $62,5^\circ$, and it is therefore most probably a paraffin-like hydrocarbon. In addition to citral, of which the quantity was found by Theulier to be 20,8 per cent., the oil contained l-limonene (proved by the tetrabromide which was prepared from it, though not in a perfectly pure state); geraniol (separated by the calcium chloride compound, and identified by oxidation into citral), and a probably laevorotatory sesquiterpene.

Vetiver Oil. In consequence of an enormous demand for our distillate, we have largely increased the manufacture of this product which is indispensable in the preparation of fine toilet-soaps. We now supply it in any quantity.

P. Genvresse and G. Langlois²⁾ have detected two compounds in vetiver oil, but these have no importance for the odour of the oil. The two oils serving for the examination originated from Bourbon and from Grasse. The neutral Bourbon oil had the specific gravity 0,993 (20°), the optical rotation $+23^\circ 43'$ (in alcoholic solution); with the oil from Grasse the specific gravity was 1,012 (20°), and the rotatory power $+27^\circ 9'$. The last-named oil had an acid reaction. When submitted to steam-distillation, only one-third of the total oil passed over, of which one part was specifically lighter, and the other heavier than water. The former consists chiefly of a sesquiterpene $C_{15}H_{24}$, vetivene, a colour- and odourless liquid of the boiling point 262° to 263° (740 mm, 135° at 15 mm), the specific gravity 0,932 (20°), and the optical rotation $+18^\circ 19'$. It absorbs without solidifying 4 atoms bromine, whereby it acquires a blue colour. The heavier portion of the oil consists essentially of a sesquiterpenic alcohol $C_{15}H_{26}O$, vetivenol, a thickish bright-yellow odourless body with the following physical constants: boiling point 169° to 170° (15 mm), specific gravity 1,011 (20°), optical rotation $+53^\circ 43'$ (in alcoholic solution). When the alcohol is treated with acetic anhydride, it forms an acetate; anhydrous

¹⁾ Bull. Soc. chim. III. **27** (1902), 1013.

²⁾ Compt. rend. **135** (1902), 1059.

oxalic acid acts upon it with formation of the above-mentioned sesquiterpenic hydrocarbon vetivene. The distillation residue contains, in addition to vetivenol, an acid or mixture of acids, a white, viscid mass, acquiring a brown colour when exposed to the air, which yields a soluble potassium salt. The body which bears the characteristic odour of vetiver oil is an ester of this acid and of vetivenol, which is very easily saponified already by water.

Wintergreen Oil. According to American reports, the stocks have been greatly reduced by an uninterrupted strong demand, and the prices show an upward tendency. Since the lowest quotation in January 1902 at \$ 1.45, they have gradually risen to \$ 1.75. The production during last year has been scanty, as even the higher prices paid are not remunerative, in view of the high wages. This state of affairs is the direct consequence of the competition of the artificial oil, which since the great drop in the prices of salicylic acid can be supplied at an absurdly low price, and which, also as regards quality, will be acknowledged by every unbiassed judge to be equal to the natural oil.

Methyl ester of salicylic acid, as is well known, is present in the roots of many polygalaceae. According to recent observations made in the agriculturo-chemical Laboratory of the Botanic Garden of Buitenzorg¹⁾, it also occurs in the saprophytes *Epirrhizanthus elongata* Bl. and *Epirrhizanthus cylindrica* Bl., which also belong to the family of polygalaceae. The pulp of *Coffea liberica* and *Coffea stenophylla* also contains this ester, but, strange to say, it is not present in the pulp of *Coffea arabica*. On the other hand, methyl ester of salicylic acid has been detected in the pulp of hybrids between *Coffea arabica* and *Coffea liberica*.

Wormwood Oil. The American distillate is still quoted at a disproportionately high price, and moreover does not now give satisfaction in the quality. For this reason we prefer to wait until normal conditions return once more. Of French oil, on the other hand, a choice selection is available. First in point of quality stands the oil distilled from the cultivated herb in the neighbourhood of Paris; our quotation refers to this oil.

Ylang-Ylang Oil, "Sartorius" I. The hopes expressed by our friends at Manila, that the rise of 50 marks per kilo, which was put in force last autumn, might be sufficient, have unfortunately not been realised; on the contrary, they were absolutely compelled to raise the price by another 50 marks, and they assure us most

¹⁾ Annual Report 1901, 58.

positively that even now their expenses are not covered. There is such a competition in the purchase of the flowers, that the prices are driven up beyond all limits, and the factories will be forced to transfer the distillation to the interior of the island, so as to escape from the conditions which prevail in Manila. On the other hand, the enormous prices paid for the flowers may induce the producers to enlarge the plantations, which would sooner or later lead to an increased supply of flower-material. We have received the most binding promises from our friends, that, as soon as this drop in the values takes place, the prices will be reduced as far as possible. But for the present this is out of the question, for there is everywhere a lack of really fine qualities, and the demand is so large, that we could easily dispose of double the quantity of the Sartorius brand, of which we have as hitherto the sole rights of sale. Our importation during the year 1902 amounted to 49 cases = 250 kilos and 800 grams.

Ylang-Ylang Oil, "Schimmel & Co." (German Patent No. 142 859). The favourable state of affairs of the natural flower-distillate has promoted the sale of our synthetic product, and has helped to introduce it into several perfumery-factories. When once it is introduced, it acquires a permanent place, for by the improvements which it has constantly undergone by the discovery of new constituents of the natural oil, it has approached the latter so closely in point of quality, that it can only be distinguished with difficulty from the finest brands. At the present moment it requires already an expert knowledge to detect any difference, and it is really astonishing, in view of the enormous difference in the prices, that here and there clients still hesitate to adopt the artificial oil.

In any case, it should now no longer be judged by previous trials, but new comparisons should be made in order to obtain a correct idea of the quality and fineness of our present product. For since its introduction we have detected a whole series of the most important constituents, which, added in the proper proportion, impart to the artificial oil in a constantly higher degree the stamp of genuineness and truth to nature.

When in the year 1895 we undertook the examination of ylang-ylang oil, only the following bodies were known as constituents of this oil: linalol, geraniol, p-cresol methyl ether, acetic acid, and benzoic acid in the form of esters¹⁾.

It was, of course, impossible to imitate ylang-ylang oil artificially with these bodies alone, and the further we advanced with our work, the clearer it became, that ylang-ylang oil belongs to that class of oils,

¹⁾ Compt. rend. **76** (1873), 1482; Reychler, Bull. Soc. chim. III. **11** (1894), 407, 576, 1045; **13** (1895), 140.

which owe their aroma to the joint action of a large number of different bodies.

In addition to the above-named already known constituents, we have either proved the presence of the following important aromatic bodies with absolute certainty and isolated them, or have indicated their presence as very probable¹⁾. They are: —

Pinene, creosol, eugenol, isoeugenol, eugenolmethyl ether, benzyl alcohol, benzyl acetate, benzyl benzoate, methyl ester of benzoic acid, methyl ester of salicylic acid, methyl ester of anthranilic acid, and further, an odourless sesquiterpenic alcohol melting at 138°.

In order to protect this discovery we have on 23rd September 1901 applied for letters-patent.

Novelties.

In November last year we received from Professor Zimmermann, who directs the Botanical Garden at Amani in German East Africa, a sample of wood obtained from a species of tree which is there indigenous. The red-brown wood, in places covered with brilliant crystals, diffused a penetrating skatol-like odour. In order to obtain the odorous substance, the pieces of wood were washed several times with ether. After distilling off the ether, a brown crystalline mass remained behind, which was then distilled out with steam. In this manner we obtained from 112 grams wood, 1,2 gram = about 1 per cent. of white crystals with an intense skatol-odour, which melted at 95°. These are consequently identic with skatol. With hydrochloric acid they formed a hydrochloride melting at 168°. As it was usual to consider skatol essentially as a secretion of the animal organism, the fact, here confirmed, of the presence of not at all unimportant quantities of this powerfully smelling body, is especially interesting.

Skatol was observed for the first time in a plant by Dunstan²⁾. He found it in a sample of the wood of *Celtis reticulosa*, collected by Daniel Hanbury and deposited at the museum of the Pharmaceutical Society of London. This tree occurs in Java, Ceylon, and the East Indies. The fresh wood of this tree is also said to have a penetrating and abominable odour.

Up to the present it has not yet been possible to determine the botanical origin of the tree indigenous to East Africa, from which the wood examined by us was obtained.

¹⁾ Report April 1896, 62; April 1899, 9; October 1901, 54; April 1902, 64.

²⁾ Pharmaceutical Journal 19 (1899), 1010.

We have further received from Amani a white-coloured wood, which has a much fainter odour of skatol, and which at the same time smells like linalol. Its botanical origin is also unknown.

Professor Zimmermann makes the following remarks on the subject:

"The wood of this species of tree has in the fresh state a fairly faint and not exactly disagreeable odour. Only when it has reached a certain state of decay it commences to smell strongly and disagreeably, but in a further stage of decomposition it again becomes odourless. It may be assumed that the fresh wood already contains a substance from which through decay the malodorous substance originates."

This observation, which at any rate is very interesting, deserves to be continued further. As we have as yet been unable to obtain a sufficient quantity of material, we have not yet been in a position to make a chemical examination of the white species of wood.

Notes of recent scientific work concerning terpenes and terpene derivatives.

The disinfecting action of essential oils and their constituents has lately been the subject of several examinations.

Calvello¹⁾ has made comparative tests regarding the bactericide properties of oils of thyme and cinnamon, and other oils, as compared with a 1 per cent. solution of mercuric chloride, and he has found that a 7 to 8 per cent. emulsion of cinnamon oil, or an 11 per cent. solution of thyme oil, in washing the hands, has the same sterilising action as the solution of mercuric chloride, without possessing the disagreeable secondary properties of the latter. The most powerful action is obtained with a 9 per cent. emulsion of cinnamon oil, which effects complete sterilisation.

Marx²⁾, in continuation of previous work by Konradi, has examined terpineol, heliotropin, vanillin and other aromatic bodies for the same purpose.

The development of pathogenic germs, such as the spores of anthrax and *Staphylococcus pyogenes aureus*, is arrested by the above-named substances. A 1 per cent. solution of terpineol destroyed *Anthrax* after 1 hour, and in a 10 per cent. solution it had the same effect on *Staphylococcus*; nitrobenzene effected the same result in a 10 per cent. solution only after 24 hours. Specially powerful is the action of terpineol in combination with soft soap. In bacteria-emulsion the above-mentioned substances, — and preferably again terpineol — effect agglutination,

¹⁾ Pharm. Ztg. **47** (1902), 759.

²⁾ Centralbl. f. Bakteriöl. und Parasitenk. **33**, I (1903), 74; according to Chem. Repert. **27** (1903), 28 and Apoth. Ztg. **18** (1903), 7.

the cause of which is attributed to the oily consistency of the substances, which, however, does not seem to come under consideration for the actual destruction. Marx rather thinks that the bactericide action is due to the capacity of the aromatic substances of rendering oxygen active, and supports this view by the observation that terpineol, (either in the substance or in the form of vapour) almost immediately liberates iodine from potassium iodide, an occurrence which with heliotropin and vanillin only takes place after several hours. The bactericide action stands, according to its degree, in direct relation to this activating power.

The fate of a number of terpenes and camphors in the animal organism has been further traced¹⁾ by Hildebrandt²⁾ and also by Fromm, Hildebrandt and Clemens³⁾. According to the former, carvone yields a combined glycuronic acid, which, on being split up with sulphuric acid, does not yield the solid oxycarvone found by Harries⁴⁾ (or the isomeric diketone formed from the latter), but an oily oxidation-product which could not be further identified. Santalol showed a behaviour which differed completely from the observations hitherto made. It appeared from the analysis of the potassium salt of the combined glycuronic acid, that during the passage through the animal body, the santalol molecule had undergone a decided diminution, as it was proved that the formula belonging to the term split off by acids, was $\text{COOH} \cdot \text{C}_9\text{H}_{16} \cdot \text{OH}$. If it is accepted with Hildebrandt, that the carboxyl group is formed by oxidation of a methyl group, it would be possible to express the loss suffered by the santalol molecule, by the splitting off of the group C_5H_6 . By means of a modified method of examination (precipitation of the alcoholic solution of potassium salt with basic acetate of lead), the author succeeded in proving, for a series of other compounds, such as fenchone, thujone, and others, an oxidation with formation of a carboxylic acid, in addition to the hydration previously observed. With compounds of the so-called "pseudo-class" of terpenes (Semmler), such as for example sabinene and sabinol, only a hydroxylation was observed. Contrary to p-cymene which in the animal body is converted into cumic acid, there was observed with m-cymene the occurrence of a combined glycuronic acid.

A peculiar departure from the regularities hitherto observed was detected with the product of conversion obtained after administration of camphene. On splitting up, a liquid body of the formula $\text{C}_{10}\text{H}_{16}\text{O}$ was obtained, which was at first regarded as an alcohol, and was called

¹⁾ Compare Report April 1902, 84.

²⁾ Zeitschrift für physiologische Chemie **36** (1902), 441 and 452.

³⁾ Zeitschrift für physiologische Chemie **37** (1903), 189.

⁴⁾ Berliner Berichte **34** (1901), 2105.

"camphenol". On closer examination it was, however, recognised as an aldehyde, and it was found possible to prove its identity with the camphenilanic aldehyde of the melting point 68° to 70° , produced by Bredt and Jagelki¹⁾ from camphene and chromyl chloride. The remarkable formation of this body is explained in this manner, that camphene adds two hydroxyls, and the camphene glycol formed appears in the urine combined with glycuronic acid, but during the decomposition with acids is again split up, and is converted, with loss of water, in the manner indicated by Bredt, into camphenilanic aldehyde.

The examination carried on by us to ascertain in how far the refractive index of essential oils may be employed for the purpose of judging their quality and purity, a matter to which we referred about a year ago²⁾, is now approaching completion. The figures which we have collected on this subject, a material of a fairly voluminous character, will be published in another place; here, we will only state in anticipation, that by this systematic examination we have by no means been converted, and that we quietly remain on the standpoint hitherto occupied. We do not deny that the determination of the indices of refraction of fractions of essential oils may be used with advantage for the detection of adulterations, and we will even supply further proofs in confirmation thereof, but for the rest we adhere to our opinion, that the time-honoured factors for judging the value, such as specific gravity, rotatory power, solubility in alcohol etc., are fully sufficient to distinguish pure oils from adulterated, and good ones from inferior oils.

The use of the iodine-addition as a method for testing essential oils has been repeatedly proposed, but the results obtained by individual investigators have proved beyond doubt that this method is not suitable for the purpose of ascertaining the quality of an essential oil. In spite of this, the method has recently again been rescued from the oblivion into which it had not undeservedly fallen, by Messrs. Sanglé-Ferrière and Cuniasse, who have employed it in the analysis of various preparations of absinthe³⁾ for the quantitative estimation of the essential oils therein contained. Now with the view of rendering the use of this formerly-employed method more common, and to adopt it as a general method for ascertaining the quantity of essential oil in liqueurs etc., the authors have determined the iodine-absorbing capacity of a whole number of essential oils which they had previously

¹⁾ Liebig's Annalen **310**, (1900), 116.

²⁾ Report April 1902, 82.

³⁾ Nouvelle méthode d'analyse des absinthes. Paris 1902, publ. by Ch. Dunod. Compare Chem. Centralblatt **1903**. I, 543.

tested for their purity by determining the physical constants and the solubility in alcohol¹⁾. The process which they thereby employed does not differ in any marked degree from that of Hübl, which is in use for the estimation of the iodine number of fatty oils. The accurately-weighed oil was dissolved in 80 per cent. alcohol, and that solution mixed with 15 to 20 cc of an alcoholic solution of iodine and mercuric chloride; after standing for exactly three hours, the excess of iodine was titrated back with deci-normal solution of sodium hyposulphite.

Messrs. Sanglé-Ferrière and Cuniasse, however, are of opinion that the iodine numbers communicated by them can not only be used with advantage for the quantitative estimation of essential oils in liqueurs or generally in alcoholic solutions, but that they can also serve for the identification and detection of adulterations of essential oils.

Assuming that the above-mentioned method really gives uniform values, it is not quite clear how from the iodine number ascertained, the content of essential oil of for example a liqueur can be found, for it is highly questionable whether the essential oil whose presence is suspected by the odour and taste, is the only representative of this class of bodies. It may be predicted with certainty that the results, in the case of mixtures, cannot be very favourable, as the essential oils do not all possess the same capacity of absorbing iodine. If the essential oil is to be estimated according to quantity, it would seem to us that Mann's method described on page 10 of our Report of October 1902, is far more suitable.

L. Balbiano and V. Paolini²⁾ have made use of an oxidising agent which had hitherto been hardly employed at all in the terpene chemistry, viz., mercuric acetate. The experiments made by them differ in so far from those of Tafel³⁾ — who allowed the same compound to act in the heated state in a closed tube on other bodies — that a solution of mercuric acetate at ordinary temperature is allowed to react slowly on hydrocarbons, olefinic phenol ethers, etc. We reproduce here briefly the results obtained by this method. In the oxidation of pinene with a saturated solution of mercuric acetate during 7 to 8 days, there results as reaction-product, an almost colourless, thickish oil whose odour reminds of camphor, of the formula $C_{10}H_{16}O_2$, i. e. a dioxypinene. It has the specific gravity 1,069 (0°) and boils at 5 mm pressure at 145°, at 20 mm at 170° to 171°. Its property of forming on the one hand with hydroxylamine an oxime of the melting point 138,5°, with semicarbazide

¹⁾ Journ. de pharm. et de chim. VI. 17 (1903), 169.

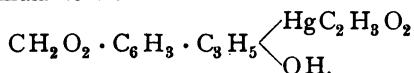
²⁾ Berliner Berichte 35 (1902), 2995.

³⁾ Berliner Berichte 25 (1892) 1619.

a semicarbazone of the melting point 180° , and on the other hand with carbanil a phenyl urethane, proves that it is here a question of a ketonic alcohol. The absorption of 2 atoms bromine shows that the product contains a double linking. Oxidation with permanganate in acid solution converts the dioxypinene into a lactic acid $C_8H_{12}O_4$ of the melting points 68° to 69° and 89° respectively, which is identic with terpenylic acid.

When anethol is oxidised with mercuric acetate, it yields a glycol $CH_3O \cdot C_6H_4 \cdot C_3H_5(OH)_2$ of the melting point 98° , which chromic acid converts into anisic acid. The diacetyl derivative of the glycol, a thickish oil, boils at 41 mm pressure at 210° .

Whilst isosafrol on treatment with mercuric acetate yields an oxidation product, safrol does not yield one, but, on the other hand, a mercuric compound occurs which is separated out, according to the length of time during which the reagent is allowed to act, either as a syrup, or as a white crystalline body. The authors give the following constitutional formula to it:



In the same manner a mercuric compound is obtained from camphene. As the authors do not give any further particulars of the manner of production or the properties of this body, and do not announce a continuation of their examination, and as we were anxious to render this reaction, if possible, available for the detection of camphene in essential oils, we have occupied ourselves with the examination of this compound. We worked under the same conditions as those given by Balbiano and Paolini for the pinene oxidation. The camphene was dissolved in an equal volume benzene. The separated compound, which was apparently of a crystalline character, was washed with water, alcohol and ether, in which it is insoluble, and was thereby obtained as a pure white, dust-like powder. After unsuccessful attempts to regenerate camphene from it by boiling with water or alkalies, we succeeded in decomposing it with hydrogen sulphide. For this purpose the powder was suspended in water, and hydrogen sulphide introduced into this suspension for 4 to 5 hours, with frequent shaking. From the black compound which was filtered off and washed, a quantity of camphene approximately the same as that employed could be isolated by steam distillation. After recrystallisation from alcohol, the camphene melted at 49° to 50° . Its boiling point was found as 159° to 160° .

The next step was to submit to this reaction an oil which was believed to contain camphene by reason of the isborneol reaction obtained with it, but from which no camphene as such had as yet

been isolated. Up to now it had frequently been necessary to be content with Bertram's isoborneol reaction alone, for the purpose of detecting the presence of camphene in essential oils. But as the occurrence of this reaction might also be due to the presence of a hitherto unknown hydrocarbon, it was desirable to supply the proof by isolating the solid hydrocarbon. We found a welcome subject for examination in the first runnings of Ceylon citronella oil, which, judging from the results obtained with the isoborneol reaction, should contain large quantities of camphene. We used for this purpose the portions passing over between 158° and 162° . The mercuric compound separated off was purified and decomposed in the above-described manner. Strange to say, it was found extremely difficult to isolate the camphene with water vapour from the decomposed compound. We believe that this was solely due to causes of a mechanical nature, for as long as the steam distillation was continued, small quantities of camphene distilled over. Melting and boiling points agreed with those of pure camphene. For further identification we converted the camphene into isoborneol, whose melting point we found at 212° .

Hydrocarbons.

Pinene. According to the German Patent No. 134553, one of the substances formed by the action of oxalic acid on pinene is camphor. Schindelmeiser¹⁾ has not found this statement confirmed; as chiefly esters of the inactive borneol are obtained.

Camphene. Konowaloff and Kikina²⁾ have obtained nitro-compounds by heating dihydrocamphene and pinene hydrochloride with nitric acid of the specific gravity 1.12. The former yielded chiefly a secondary nitro-body of the melting point 125° to 129° , which on reduction with zinc and hydrochloric acid yielded an amine of the melting point 65° to 130° , and boiling at 194° to 204° . It was more difficult to nitrate pinene hydrochloride; it yielded a mixture of solid (secondary) and liquid (primary and secondary) derivatives. These observations lead to the conclusion, that camphene, camphor, and pinene hydrochloride contain a CH-group, to which no methyl group is attached.

Fenchene. In a long publication which has recently appeared³⁾, J. Kondakow returns to Wallach's explanation of the history of fenchene, mentioned on page 91 of our last year's October Report.

¹⁾ Journ. d. russ. phys.-chem. Ges. **34** (1902), 954; according to Chem. Centralbl. **1903**, I, 515.

²⁾ Journ. d. russ. phys.-chem. Ges. **34** (1902), 925; according to Chem. Centralbl. **1903**, I, 512.

³⁾ Journ. f. pract. Chemie II. **67** (1903), 94.

In that publication he again claims priority for having accurately defined the constitution of the various hydrocarbons $C_{10}H_{16}$, formed from fenchyl alcohol and fenchyl chloride respectively. He is further of opinion, that, as he had conceived the idea of studying the isomerisation of secondary hydroaromatic alcohols into tertiary, he had also the right to include fenchyl alcohol in the sphere of his examinations, and that therefore there could be no question of an unauthorised invasion of Wallach's sphere of action.

With regard to the remark made by us in the same place, that zinc chloride as a substitute for sulphuric acid in the hydration of hydroaromatic hydrocarbons had been used by Ertschikowsky long before Kondakow, we wish to state, in accordance with a communication made by the latter¹⁾, that the experiments in question were made by Ertschikowsky at the instigation of Kondakow. For this reason, Ertschikowsky cannot be designated as the one to whom the priority for the use of this method is to be credited.

Phellandrene. According to a previous statement by Pesci, when phellandrene nitrite is reduced with zinc and glacial acetic acid, a diamine boiling at 209° to 215° is formed, which is distinguished by a platinum double salt almost insoluble in water. As Wallach has already established, phellandrene nitrite from eucalyptus oil yields, in addition to non-volatile basic compounds, a base which not only boils 40° to 50° higher than stated by Pesci, but which also shows a totally different behaviour. An examination recently made by Wallach²⁾, in which original preparations by Pesci were available for comparison, has now shown that the compounds which Pesci had obtained from the phellandrene of oil of water fennel, differ from those which can be prepared from the phellandrene of Australian eucalyptus oil. This is all the less remarkable, as O. Schreiner³⁾ has meanwhile called attention to the fact, that from the phellandrene of eucalyptus oil nitrites of different melting points can be obtained.

If the phellandrene nitrites, obtained on the one hand from eucalyptus phellandrene, and on the other from the phellandrene of water fennel, are reduced according to the method indicated by Pesci, there are obtained from both nitrites diamines which boil at 250° , but which in respect of the formation of salts behave in a totally dissimilar manner. The phellandrene diamine from eucalyptus oil namely yields a difficultly soluble monohydrochloride and a readily soluble platinum double salt; the diamine from oil of water fennel, on the other hand, yields a readily soluble hydrochloride, and a platinum double salt which is

¹⁾ Journ. f. pract. Chemie II. **66** (1902), 479.

²⁾ Liebig's Annalen **324** (1902), 269.

³⁾ Compare Report October 1901, 61.

difficult to dissolve, and these have the properties ascribed to them by Pesci. With regard to the boiling point of the base, however, Pesci has been in error, for the latter lies at about 260° , i. e. about 50° higher than would be expected from Pesci's statements. But it is correct that, as Pesci mentions, in the reduction of the phellandrene nitrites, in addition to the volatile diamine, also a considerable quantity of a non-volatile base is formed; the latter is still to be submitted to a more detailed examination.

Very welcome contributions to the knowledge of sesquiterpenes and sesquiterpenic alcohols have been supplied by J. Gadamer and T. Amenomiya¹⁾. These authors examined atractylol, a sesquiterpenic alcohol $C_{15}H_{26}O$ which forms the principal constituent of the essential oil of *Atractylis ovata* Thunbg., and in connection therewith also examined a number of other known sesquiterpenic alcohols and the sesquiterpenes formed therefrom by loss of water.

Atractylol, obtained in the pure state by crystallisation from petroleum ether at a temperature much reduced by means of solid carbon dioxide and ether, possesses a faint odour which when much diluted reminds of lilies of the valley; it melts at 59° , boils at atmospheric pressure without decomposition at 290° to 292° , and is optically inactive. As follows from the behaviour of atractylol towards phenyl isocyanate, and from acylation tests, it must be considered a tertiary alcohol; this view also agrees with the fact that the alcohol, when treated with water-abstracting substances, such as potassium hydrosulphate, is very readily converted into a hydrocarbon $C_{15}H_{24}$ atractylene. When freshly prepared this represents a fairly mobile liquid with a cedar-like odour, boiling point at 10 mm pressure chiefly at 125° to 126° ; $d_{15}^{20} = 0,9101$, and $n_{D20} = 1,50893$, which when kept polymerises, becomes viscid, and acquires a lemon-like odour. A similar polymerised product is formed when atractylene is produced from atractylene dihydrochloride by boiling with aniline. To the pure non-polymerised hydrocarbon belong two ethylene-linkings, as appears from its behaviour towards bromine and hydriodic acid, whilst the atractylene regenerated from the dihydrochloride represents essentially the polymerised compound, which also differs by its slightly dissimilar physical constants from the hydrocarbon obtained by means of potassium hydrosulphate. An attempt to attach water to atractylene, and to regenerate the alcohol, remained unsuccessful; it was equally impossible to obtain a crystallised nitrosochloride for the purpose of identification.

As already mentioned, the authors, in connection with their examination of atractylol and atractylene, publish communications on

¹⁾ Archiv der Pharm. 241 (1903), 22.

caryophyllene, patchoulene, guajene, and the alcohols belonging thereto, and finally also on oil of carline thistle, but these in the main only confirm already-known facts concerning these compounds.

Of the chemistry of Para caoutchouc little is known. Contrary to other work of older date, Weber¹⁾ held the opinion that caoutchouc represented an aliphatic polyterpene with two double linkings each on one molecule $C_{10}H_{16}$, as he obtained from it tetrahalogen compounds of the formula $(C_{10}H_{16}X_4)_n$. Harries²⁾ supports this view. In the degradation of the caoutchouc molecule he obtained, by means of nitrous acid, under various conditions, nitrosites of a dimolecular terpene, which resembled the nitrosites of dimyrcene, a polymerisation-product of the aliphatic terpene myrcene. The process of reaction appears to be accomplished thus, that first of all nitrosites of a tetraterpene are formed, and on further oxidation diterpene derivatives. In the pyrogenic polymerisation of cyclic terpenes, such as limonene, dipentene, and others, no bodies were obtained which under the same conditions yielded addition-products with N_2O_5 . Dipentene which is stated to occur in large quantity in the distillation of caoutchouc, but which was only obtained in a yield of about 15 per cent. is, according to Harries, produced by secondary formation from isoprene or the hypothetical diisoprene, and not from caoutchouc direct.

Alcohols.

For the detection of bodies containing hydroxyl (alcohols, phenols, or oximes) Tschugaeff³⁾ recommends that the substance to be examined be brought into reaction with organic magnesium compounds of the formula $R \cdot Mg \cdot I$, such as $CH_3 \cdot Mg \cdot I$. In the presence of a hydroxyl-group methane is formed according to the equation $CH_3MgI + R \cdot OH = RO \cdot MgI + CH_4$. As these Mg-organic compounds of alcohols etc. are non-volatile, this method can also serve for their separation from volatile indifferent bodies, such as hydrocarbons, as the latter can be distilled off in vacuo.

In the "Archiv für experimentelle Pathologie und Pharmacologie" vol. 48 (1902), 223, E. Erdmann reports more in detail on the pharmacological action of fufur alcohol⁴⁾.

The experiments on animals and on men show that this constituent of essential oil of coffee possesses toxic properties which are not

¹⁾ Berliner Berichte 33 (1900), 779; 35 (1902), 1947.

²⁾ Berliner Berichte 35 (1902), 3256; 4429.

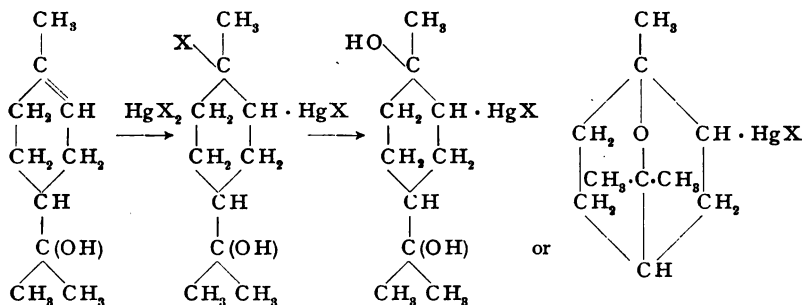
³⁾ Chemiker Zeitung 26 (1902), 1043.

⁴⁾ Compare also Report October 1902, 31.

inconsiderable, and it would therefore appear by no means impossible, that the effects on the respiration and pulsation which occur when coffee is partaken of, must in part be attributed to the presence of furfur alcohol. Further information on the cause of the action of coffee may possibly be obtained from the pharmacological examination of the nitrogenous substance contained in oil of coffee. In apparent contradiction herewith are the statements by K. B. Lehmann and G. Rohrer¹⁾, who have also occupied themselves with the question of the pharmacological action of distillates from coffee and tea. They confirm by new experiments a previously obtained result, according to which neither the coffee- nor the tea-distillate exerts any action worth mentioning, either temporary or permanent, whatever.

Manasse²⁾ has extended the well-known synthesis of aromatic oxyalcohols from phenols and formaldehyde³⁾ to a number of other phenols, such as eugenol, thymol, carvacrol and o-oxyquinoline.

Sand and Singer⁴⁾ have recently enlarged the previous work by Hofmann and Sand on the formation of mercuric compounds from unsaturated bodies and mercuric salts, by adding to it terpineol and dimethyl heptenol. They found here also, that salts of mercury HgX_2 united in such manner with the double linking, that the group HgX becomes attached to the carbon atom richer in hydrogen; the other attached group X can be readily split off by hydrolysis, and the conversion which takes place is either extra-molecular with substitution by the OH-group, or intra-molecular with loss of water and formation of an oxide-like compound. The following formula of the process of the reaction in the case of terpineol may serve to elucidate this:



¹⁾ Archiv für Hygiene **44** (1902), 202; according to Chem. Centr. Blatt **1902**, II, 1067.

²⁾ Berliner Berichte **35** (1902), 3844.

³⁾ Berliner Berichte **27** (1894), 2409. — German Patent No. 85588.

⁴⁾ Berliner Berichte **35** (1902), 3170.

According to the conditions selected, there are, therefore, obtained the Hg-salts either of cineol, or of two isomeric trans-terpins; by reduction with sodium amalgam or electrolytic hydrogen, trans-terpin of the melting point 156° can be obtained from the latter.

The reaction took place in the same manner when applied to the dimethyl heptenol obtainable from methyl heptenone with $\text{CH}_3 \cdot \text{Mg} \cdot \text{I}$.

Minguin and de Bollemont¹⁾ have recently continued their work (discussed in our previous Report²⁾ on the rotation of the esters of lævo-borneol, and have extended it to the esters of lævo-isoborneol. It was hereby found that the molecular rotatory power only becomes constant from the ester of valerianic acid, a fact which is attributed to the action of the lower acids splitting off water, with formation of inactive camphene, and the esterification of the latter into inactive isobornyl ester. The authors are of opinion that their supposition is confirmed by the fact, that the rotation of the isoborneol obtained from the esters by saponification is only constant in the preparation made from the valerianate, and that the lower homologues always yield isoborneol of constantly decreasing rotatory power. A similar regularity of the rotatory power could not be detected in homologue alkyl esters of camphocarbonic acid, presumably owing to the occurrence of compounds of the isomeric keto- and enol-forms, or of stereomerides.

Substituted glycollic esters of borneol and menthol have been produced by Einhorn and Jahn³⁾ by allowing bases, such as diethylamine and amido camphor, to act on the chloro-acetic acid esters of these alcohols. The diethyl glycollic ester of menthol may possibly be interesting from a therapeutical point of view, as it forms a readily soluble hydrochloride, and in the organism splits off menthol.

J. Kondakow and J. Schindelmeiser⁴⁾ report on some derivatives of menthol. Like other secondary hydroaromatic alcohols, menthol also yields no uniform body when it is converted into menthyl halogen compounds, but on the contrary forms mixtures of secondary and tertiary compounds, whose quantities vary according to the reagent employed (phosphorus halogen compounds or concentrated acids of hydrohalogen), and to the temperature at which the action thereof takes place. If alcoholic alkali is allowed to act on these mixtures, the tertiary menthyl halogen compounds split off hydrohalogen much more

¹⁾ Compt. rend. **136** (1902), 238.

²⁾ Report October **1902**, 94.

³⁾ Archiv d. Pharm. **240** (1902), 644.

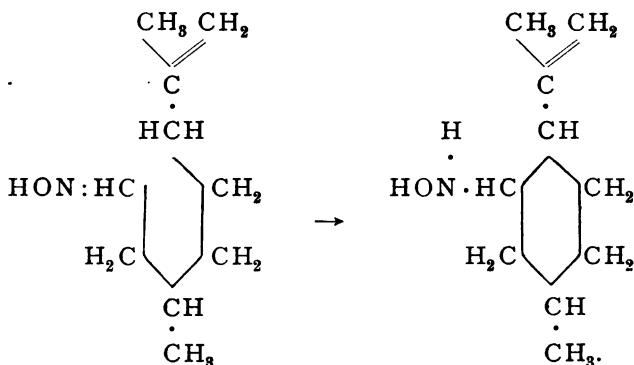
⁴⁾ Journ. f. prakt. Chemie II. **67** (1903), 193.

readily, with formation of hydrocarbon, than the secondary compounds, which are partly again obtained without change.

Kondakow and Schindelmeyer have made a more detailed examination of the menthyl bromide, formed by the action of phosphorus pentabromide or concentrated hydrobromic acid on menthol, and find the above statement confirmed. Of much interest is the observation, that the menthene which is formed from tertiary menthyl bromide, cannot be completely converted by Reychler's process (by the action of trichloro-acetic acid) into tertiary menthol. The small portion of the hydrocarbon which remains unattacked has a somewhat different odour, and also boils higher, than the ordinary menthene; it is possible that it represents a pseudo-menthene.

Aldehydes.

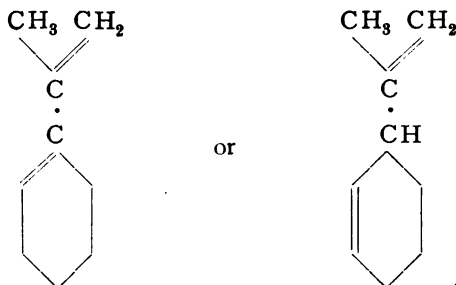
Citronellal. If citronellal oxime is mixed at a much reduced temperature with several times its weight of about 50 per cent. sulphuric acid, the mixture which is at first clear, becomes cloudy (as F. Mahla¹) observed) when left standing for several hours, and the acid liquid now contains a base $C_9H_{19}ON$, which is formed from the oxime by formation of a ring with simultaneous displacement of one atom of hydrogen:



The citronellal oxime has consequently changed into a $\Delta^{8(9)}$ -oxamino-3-menthene. If sodium nitrite is allowed to act on this base in the presence of oxalic acid in aqueous solution, the one atom of hydrogen of the $NH \cdot OH$ -group is replaced by NO , and a nitroso-oxamino-menthene is obtained as a crystallised compound melting at 52° . Under the influence of heat or dilute acids this compound is readily decomposed with liberation of nitrous oxide N_2O , by which there is

¹) Berliner Berichte 36 (1903), 484.

formed, in addition to an optically inactive alcohol $C_{10}H_{20}O$ with a terpeneol-like odour, a hydrocarbon $C_{10}H_{16}$, which in view of its origin must be considered as $\Delta^2, 8(9)$ -, or still more probably as $\Delta^3, 8(9)$ -menthadiene:

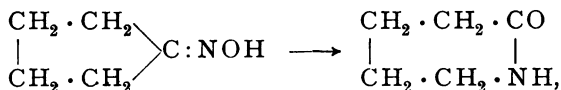


The hydrocarbon is dextrorotatory, like citronellal; it boils at 9 mm pressure between 75° and 80° , and has the specific gravity 0,8491. Its odour is said to remind of anise and star-anise, but at the same time also somewhat of fennel.

Ketones.

Wallach¹⁾ has communicated a very interesting treatise on the conversion of cyclic ketones into alkamines and into non-oxygenous bases of nitrogenous cyclic systems.

The same investigator has already shown on a previous occasion, that the oximes of cyclic ketones, on conversion into the so-called isoximes, suffer a molecular rearrangement, with formation of compounds which may be considered as anhydrides of acid amides (lactams), and that in this manner it is possible to arrive partly at already known, and partly at new nitrogenous heterocyclic compounds²⁾. Thus pentanone oxime is converted into α -piperidone:



whilst from cyclohexanone and cycloheptanone oximes in a corresponding manner heterocyclic compounds with seven or eight members can be obtained.

These isoximes or lactams are now susceptible to direct reduction, preferably by the application of amyl alcohol and sodium, and it is thereby possible to arrive at non-oxygenous bases of nitrogenous cyclic

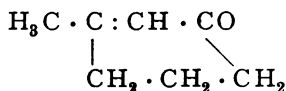
¹⁾ Liebig's Annalen **324** (1902), 281.

²⁾ Compare Report October **1900**, 74.

systems. At the same time, the reaction does not always pass off smoothly and uniformly, for the more the isoxime employed is inclined to ring-disruption (when, as is well known, fatty amido acids are formed), the smaller is the yield of non-oxygenous basic products. But moreover, there occur on reduction also oxygenous bases, i. e. alkamines, and that, in the case of higher cyclic systems, in considerable quantity. Whether with these only the reduction of the CO-group into a CHOH-group has taken place, or simultaneously also ring-disruption with formation of aliphatic amido alcohols, has not yet been definitely decided for all cases.

But in any case so much is certain, that this reduction supplies a means for obtaining the higher ring-homologues of piperidine, by which the doctrine of the nitrogenous ring-systems is enlarged in a welcome manner. For, next to the already known types tri- and tetramethyleneimine, as also the pentamethyleneimine or piperidine obtainable from α -pyrrolidone, there are now also hexamethyleneimine $(\text{CH}_2)_6\text{NH}$ and heptamethyleneimine $(\text{CH}_2)_7\text{NH}$, of which the former can be obtained from cyclohexanoneisoxime, and the latter from the isoxime of suberone.

Just as dihydroisophorone or dihydroisophorol can be converted into α -cyclogeraniolene and with the help of the latter into trimethyl cyclohexanone¹⁾, there can also be obtained (as Wallach has recently found²⁾ from methyl-1-cyclohexanone-3 from pulegone, a cyclomethyl hexenone, which differs from Knoevenagel's well-known methyl cyclohexenone



either by the position of the ethylene linking, or by that of the carbonyl.

The alcohol formed by reduction from methyl hexanone yields, when heated with zinc chloride, a methyl cyclohexene (tetrahydrotoluene) which, like α -cyclogeraniolene, forms a difficultly soluble nitrosate. On being heated with sodium methylate, the latter yields a liquid methyl cyclohexenoneoxime, which can be split up by dilute sulphuric acid. The cyclomethylhexenone thereby formed boils at 179° to 181° , and its semicarbazone melts at 207° to 208° ; it therefore certainly differs from the ketone of the above-mentioned constitution.

As was pointed out some few years ago by Rabe³⁾, aceto-acetic ester, under the influence of sodium ethylate, is attached to α , β -unsaturated

¹⁾ Compare Report October 1902, 86.

²⁾ Berliner Berichte 35 (1902), 2822. — Nachrichten der Kgl. Ges. d. Wiss. zu Göttingen 1902, 297.

³⁾ Berliner Berichte 31 (1898), 1896.

esters, ketones etc. If the addition-product is saponified and carbon dioxide split off from the acid, there is not formed a 1,5-diketone, as might be expected, but (as was recently proved by Rabe and Weiling¹⁾ with the condensation-product from aceto-acetic ester and carvone), an isomeric bicyclic ketone alcohol of the formula $C_{13}H_{20}O_2$, which on reduction with zinc and hydrochloric acid yielded a mixture of two optically active glycols. A product prepared years ago by Goldschmidt and Kisser²⁾ by condensation of the above-mentioned bodies with hydrochloric acid, in which the isopropenyl-group of the carvone-*rest* is saturated with HCl, was also examined by Rabe and Weiling³⁾. They obtained on saponification with potassium hydrate, in addition to eucarvone, a body $C_{13}H_{20}O_2$ which is isomeric and possibly identic with the ketone alcohol mentioned above. When boiled with quinoline the condensation-product split up into acetone, aceto-acetic ester and carvacrol.

The physiological action of camphocarbonic acid and its esters has recently been examined by Gottlieb⁴⁾, in continuation of the previous work by Kobert and Lapin. Whilst camphocarbonic acid itself, and also its salts, do not act on the heart and the nervous system, and pass through the body without change, the esters show in a varying degree of strength the typical spasm-provoking effect of camphor, though not quite so strongly as the latter. The effect of the amyl ester is the most powerful; it was less strong with the ethyl ester, and still weaker with the methyl ester. The physiological activity appears to be proportionate to the electrolytic dissociation of the ester; the strongly dissociated methyl ester has the least powerful action, as contrasted with the strongly acting but little dissociated amyl ester.

Oxides.

From a trivalent alcohol of the terpene-series there can be formed, by splitting off water, a ketone (as with terpineol), or a double unsaturated alcohol, or an unsaturated oxide. The latter is the case, as Semmler⁵⁾ has just reported, with the trivalent glycerine $C_{10}H_{20}O_3$, which is formed by oxidation in the cold of dihydrocarveol with a solution of potassium permanganate. Wallach⁶⁾ had already allowed sulphuric acid to act on this compound, and had thus obtained a body $C_{10}H_{16}O$, which yielded two nitrogenous derivatives with hydroxylamine.

¹⁾ Berliner Berichte **36** (1903), 225, 227.

²⁾ Berliner Berichte **20** (1887), 489.

³⁾ Berliner Berichte **36** (1903), 234.

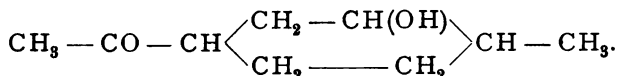
⁴⁾ Berliner Berichte **35** (1902), 3518.

⁵⁾ Berliner Berichte **36** (1903), 764.

⁶⁾ Liebig's Annalen **277** (1893), 151, and **279** (1894), 386.

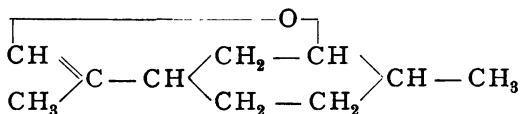
Semmler has taken up the study of these compounds which hitherto had not been examined further, and he has thereby found that the product obtained with sulphuric acid is an oxide, as it is not attacked by potassium and sodium at the boiling temperature. Its constants are: boiling point at 20 mm 95° , specific gravity 0,9647, index of refraction 1,4844, molecular refraction 45,2 (calculated 45,22 for the oxide $C_{10}H_{16}O$ with one double linking).

The dihydrocarboxide (as the author designated this oxide) yields with bromine a fairly unstable dibromide of the melting point 55° ; it is therefore unsaturated. On oxidation with a solution of potassium permanganate, an indifferent body $C_9H_{16}O_2$ is obtained which melts at 58° to 59° , and has the boiling point 144° to 145° (at 13 mm) and the specific gravity 1,0351 (at 20°). This is identical with the alcohol $C_9H_{16}O_2$ of the constitution



which Tiemann and Semmler¹⁾ had obtained direct from the dihydrocarveol-glycerine by oxidation.

From this the author deduces for the dihydrocarboxide the formula



The reactions further described also agree with this formula.

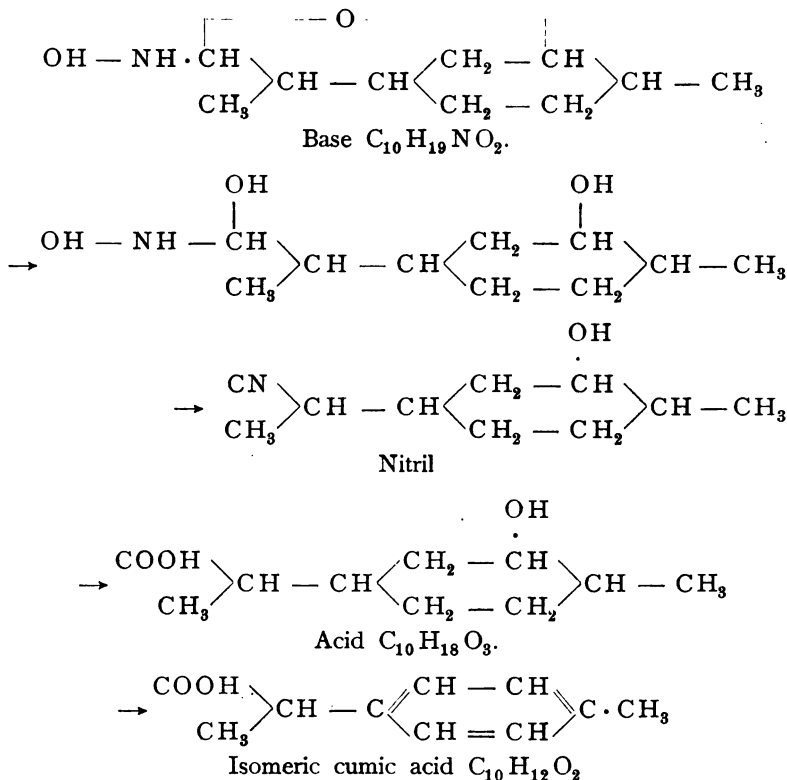
If the oxide is submitted to the action of hydroxylamine in alcoholic solution, there is obtained the basic addition-product $C_{10}H_{19}NO_2$ of the melting point 113° to 114° , which dissolves readily in dilute acids, and which is reconverted by the latter with great facility into the oxide.

The hydrochloride of the base melts at 93° , and its benzoyl compound $C_{10}H_{18}NO_2(COC_6H_5)$ at 144° . From the formation of the latter the author concludes that a hydroxyl-group is present.

If the base is heated in a tube for half an hour with alcoholic potassa to 160° , an alcoholic acid $C_{10}H_{18}O_3$ is obtained in addition to nitril. This acid is monobasic, yields with carbanil a urethane, and can be oxidised into the ketonic acid $C_{10}H_{16}O_3$, whose semicarbazone melts at 178° to 179° . If the alcoholic acid is heated with bromine water in a melting tube, an isomeric cumic acid is

¹⁾ Berliner Berichte 28 (1895), 241.

formed, which contains the carboxyl-group in the side-chain. The formation of the acid is consequently as follows: —



Borneol (Borneo camphor). This preparation, which many years ago we were the first to manufacture on a large scale, has gradually conquered an important market in the East, and, in proportion to the larger consumption, could be supplied at lower prices.

We produce it in very large quantities, and are always pleased to consider any special wishes with regard to the size of the crystals.

Citral. The prices of this body, which has been discovered by us, move in harmony with those of lemongrass oil; it is very doubtful whether they will ever return to their former level, as the demand for the above-mentioned crude material is not proportionate to the limited production, and offers have now been totally absent for some time.

There is, however, a prospect of fresh sources of supply being opened up, and a first consignment from that quarter has reached us some little time ago.

Coumarin. It seems as if the prices had now reached the lowest level, and that there is no inclination to cut the value still further. Those manufacturers who had looked for mountains of gold from this article, have probably committed a great error in estimating the turnover. Being at their wits' end, they now endeavour with American support to bring stability in the quotations.

Since the completion of our new factories we manufacture this article of the well-known exquisite quality on the largest scale.

Eugenol. The extensive manufacture of this preparation has been specially taken into consideration in our new premises. The price depends upon the quotations of cloves from time to time in force, and for this reason special arrangements will be made for contracts for large quantities.

Geraniol. With our vast installations we are in a position to supply a perfectly pure article in any quantity. The consumption would probably acquire larger dimensions if by chance the Indian geranium oil (palmarosa oil) were not now so cheap; this oil, as is well known, consists chiefly of geraniol, of which it contains 76 to 93 per cent.

Mignonette(Reseda)-geraniol. The demand for this interesting product has been so brisk, that our stock will hardly last until the new mignonette-harvest, which is gathered in August. We would earnestly request that any requirements may be specified without delay, so that the necessary quantities may be reserved.

Heliotropin. The situation has so far grown worse, that a manufacturer, whose chief merit is the ruination of this article, is unable to dispose of his stock, and now hawks it about at any price. The consumption of heliotropin has also been greatly overrated, and a senseless overproduction has taken place which now has an all the more depressing effect, as the sale of such perfumes cannot be forced, even at the cheapest prices.

At one time heliotropin was often considered poisonous. But, as will be seen from the communications in the Appendix to the present Report, piperonal is in man physiologically inactive. Its harmless character is proved by a case in which a chemist, for the purpose of suicide, took a dose of 50 cc of a concentrated alcoholic solution of piperonal (i. e. about 10 g piperonal). His condition was in no way affected even by this enormous dose.

On animals the effect is different. We would specially refer to the surprising results obtained in this connection which are quoted on pages 135 and 136.

Menthol. This article has also been carried along by the general upward movement of peppermint oil, and has been driven up to a level which has not been known for years. For crude Japanese crystals the movement was as follows: —

Cheapest quotation in July	1902, about 12/-	per lb.
average	August	14/6
"	" September	15/6
"	" October	17/6
"	" November	24/-
"	" December	25/-
"	" January 1903	24/-
"	" February	22/-

These prices are no doubt high, but they are not by any means the highest which have ever been quoted, as many people believe. In 1883 crude menthol was quoted as high as 37/- per lb.

The upward movement has partly been caused by the numerous sales in blanc which were made in June and July for forward delivery, and for which in October to December either cover had to be found at high prices, or else large differences had to be paid.

In view of the constantly growing consumption of menthol for all kinds of toilet-preparations and pharmaceutical remedies, a decline of the prices to a very low level is no doubt out of the question; but it may be found impossible to maintain the present prices, which are still high, and we cannot recommend them for larger contracts for forward delivery.

The shipments of Japanese crude menthol from Japan since 1st August 1902 were: —

To Hongkong	6900	catties
" San Francisco	6120	"
" Hamburg	4820	"
" London	3510	"
" New York	1845	"
" Seattle	1575	"
" Tacoma	1125	"
" Victoria	450	"
" Havre	135	"
" Bombay	85	"
" Madras	37	"
" Singapore	30	"

Total 26632 catties,
or about 16000 kilos.

The high prices have brought many old speculative stocks to the light in Europe, which were frequently sold below the market-price.

On account of the slight solubility of menthol and peppermint oil in water, it is often necessary to have recourse to high-priced alcoholic solutions. Dr. Crésantignes¹⁾ therefore proposes to dissolve menthol first in tincture of quillaia, and to add this solution to the water in small portions. It is stated that in this manner clear and permanent menthol-mixtures can be obtained, for example: —

Menthol.	0,15 to 0,3 g
Tinct. quillaiae	10,0 „
Aq. qu. s. ad	150,0 cc.

The following prescription is given for a mouth-wash: —

Menthol.	0,1 to 0,2 g
Tinct. quillaiae	20,0 „
Solut. acid. boric. 1 per cent.	1000,0 „

For internal use the mixtures may perhaps not be suitable, on account of the toxic properties of the quillaia-tincture.

Safrol. Nothing can as yet be noticed of the competition of the Japanese product, which some while ago was announced with such a great flourish; it appears that wise counsels have prevailed, and that the enterprise has been abandoned during the last few months, rather than let it come to a fiasco. The article is of too little importance than that its production, carried on as a separate industry, could be made remunerative. We push this article, and meet every competition where it is a question of a product of equal value.

Amyl ester of Salicylic acid. This preparation, of which we have taken up the manufacture some time ago, has found a large and varied application in the perfumery-industry. Lately it has also come into use for therapeutic purposes²⁾. According to Doyen and Chan oz the ester is only slightly poisonous, and splits up in the liver into amyl alcohol and salicylic acid. Lyonett dressed rheumatic affections with 2 to 3 g of the ester, by means of cotton-wool and gutta-percha tissue. No inflammation was ever observed. He always found afterwards that the pain and swelling had abated, but never that the remedy was not tolerated. Salicylic acid can within a short time be detected in the urine. When administered internally good results are also obtained.

¹⁾ Rep. de Pharm. 1903, Nr. 1. According to Pharm. Ztg. 48 (1903), 78.

²⁾ According to Pharm. Centralhalle 43 (1902), 637.

Santalol. This product, which, as is well known, was first introduced into commerce by us, finds a fairly large application, but it is already sold at prices which are directly unremunerative if the manufacture is carried on with care.

Terpineol. The enormous prices of American oil of turpentine have caused a hardening of the quotations of terpineol. In Austria the import-duty for this product has been raised to 1/6 d. per kilo, and as a consequence we now manufacture it at our Bodembach works.

Thymol. The ridiculously cheap quotations of this article do not call for comment in order to characterise the situation which in this case also has been brought about by overproduction. At the same time, the price of the crude material is not correspondingly lower, and especially during the last few months rather firmer.

The following statistics show that the prices of thymol have never been as low as at this moment.

We quoted: —

on 1 st April	1894:	18	marks	per	kilo
" "	"	1895:	18	"	" "
" "	"	1896:	14	"	" "
" "	"	1897:	13,50	"	" "
" "	"	1898:	13,50	"	" "
" "	"	1899:	16	"	" "
" "	"	1900:	19	"	" "
" "	"	1901:	22	"	" "
" "	"	1902:	16	"	" "
" "	"	1903:	13	"	" "

The prices of ajowan-seed (from which thymol is produced) usually depend on the sanitary conditions in the producing country, British India. They were always highest during epidemics of bubonic plague and cholera. If this factor is taken into account, the hygienic condition in India should at present be normal.

Battandier¹⁾ reports on a new occurrence of thymol. He found that the essential oil of a plant which grows in the mountainous region of Algeria, *Origanum floribundum* Munby (*O. cinereum* de Nöe), when extracted with alkali, yields one-fourth of its volume to the latter. The separated phenol crystallises almost completely when a thymol crystal is brought into contact with it, and consequently consists chiefly of

¹⁾ Journ. de pharm. et de chim. VI. 16 (1902), 536.

thymol; the small remnant of the oil which remains liquid appears to be carvacrol.

For practical purposes this new source of thymol is of no consequence, as the plant, although it is very rich in oil, is not found in large quantities.

Vanillin. The fall in the prices has made further progress since our last Report, in consequence of an increase in the production beyond all measure. There is no sensible reason for such far-going price-cutting, as it can only have the effect of bringing the article into bad repute. Unfortunately a certain doubt, that it may injuriously affect the quality, is not unwarranted, for products are met with in commerce, which in working up exhibit striking deviations from normal vanillin, and which have led to unpleasant experiences.

For this reason it is a bad plan to consider only the price when purchasing this article; on the contrary, the reliability of the manufacturer should first of all be taken into consideration. These inferior qualities are not always adulterated; they rather suffer from technical defects, which may possibly be due to a certain lack of cleanliness and care in the manufacture, or perhaps to the use of inferior solvents in the crystallisation. For the rest, according to human foresight the lowest selling price has probably now been reached, and the time may be near when the production of vanillin will be abandoned by many manufacturers as unremunerative.

Schimmel & Co.

In connection with the table for calculating from the ester numbers the percentages of alcohols of the formulæ $C_{10}H_{18}O$ and $C_{10}H_{20}O$, and of the acetates belonging thereto, which we published in our Report of October 1897, we have now drawn up a similar table for the alcohols $C_{15}H_{24}O$ (santalol) and $C_{15}H_{26}O$.

We have also provided a table for the calculation of geranyl tiglate from the ester number, as in the case of geranium oils the ester-content is usually calculated on tiglinic acid.

With regard to the formulæ employed for the calculation, and to the use of the tables, we would refer to what we stated in the above-mentioned Report, and also to the statements made by Gildemeister and Hoffmann in their work 'The Volatile Oils'¹⁾.

¹⁾ page 202.

C ₁₈ H ₃₄ O				C ₁₈ H ₃₆ O			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
1	0,47	0,39	0,39	0,47	0,40	0,40	1
2	0,94	0,79	0,79	0,94	0,79	0,79	2
3	1,40	1,18	1,18	1,41	1,19	1,19	3
4	1,87	1,57	1,58	1,89	1,59	1,59	4
5	2,34	1,96	1,97	2,36	1,98	1,99	5
6	2,81	2,36	2,37	2,83	2,38	2,39	6
7	3,28	2,75	2,76	3,30	2,78	2,79	7
8	3,74	3,14	3,16	3,77	3,17	3,19	8
9	4,21	3,53	3,56	4,24	3,57	3,59	9
10	4,68	3,93	3,96	4,71	3,96	3,99	10
11	5,15	4,32	4,36	5,19	4,36	4,40	11
12	5,61	4,71	4,76	5,66	4,76	4,80	12
13	6,08	5,11	5,16	6,13	5,15	5,20	13
14	6,55	5,50	5,56	6,60	5,55	5,61	14
15	7,02	5,89	5,96	7,07	5,95	6,01	15
16	7,49	6,29	6,36	7,54	6,34	6,42	16
17	7,95	6,68	6,77	8,01	6,74	6,83	17
18	8,42	7,07	7,17	8,49	7,14	7,23	18
19	8,89	7,46	7,57	8,96	7,53	7,64	19
20	9,36	7,86	7,98	9,43	7,93	8,05	20
21	9,83	8,25	8,38	9,90	8,33	8,46	21
22	10,29	8,64	8,79	10,37	8,72	8,87	22
23	10,76	9,03	9,19	10,84	9,12	9,28	23
24	11,23	9,42	9,60	11,31	9,51	9,69	24
25	11,70	9,82	10,01	11,79	9,91	10,10	25
26	12,16	10,21	10,42	12,26	10,30	10,51	26
27	12,63	10,60	10,83	12,73	10,70	10,92	27
28	13,10	11,00	11,24	13,20	11,10	11,34	28
29	13,57	11,39	11,65	13,67	11,49	11,75	29
30	14,04	11,79	12,06	14,14	11,89	12,17	30
31	14,51	12,18	12,47	14,61	12,28	12,58	31
32	14,98	12,57	12,88	15,08	12,68	13,00	32
33	15,45	12,96	13,29	15,55	13,08	13,41	33
34	15,91	13,35	13,71	16,02	13,48	13,83	34
35	16,38	13,75	14,12	16,50	13,88	14,25	35
36	16,85	14,14	14,54	16,97	14,27	14,67	36
37	17,32	14,54	14,95	17,44	14,76	15,09	37
38	17,79	14,93	15,37	17,91	15,06	15,51	38
39	18,25	15,32	15,78	18,38	15,46	15,93	39
40	18,71	15,71	16,20	18,86	15,86	16,35	40

C ₁₅ H ₂₄ O				C ₁₅ H ₂₆ O			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
41	19,18	16,10	16,62	19,33	16,25	16,77	41
42	19,65	16,50	17,04	19,80	16,65	17,19	42
43	20,12	16,89	17,46	20,27	17,05	17,61	43
44	20,59	17,28	17,88	20,74	17,44	18,04	44
45	21,05	17,68	18,30	21,21	17,84	18,46	45
46	21,52	18,07	18,72	21,69	18,24	18,89	46
47	21,99	18,46	19,14	22,16	18,63	19,32	47
48	22,46	18,85	19,56	22,63	19,03	19,74	48
49	22,93	19,25	19,98	23,10	19,43	20,17	49
50	23,39	19,64	20,41	23,57	19,82	20,59	50
51	23,86	20,03	20,83	24,04	20,22	21,02	51
52	24,33	20,42	21,26	24,51	20,62	21,45	52
53	24,80	20,82	21,68	24,99	21,01	21,88	53
54	25,26	21,21	22,11	25,46	21,41	22,31	54
55	25,73	21,60	22,54	25,93	21,81	22,74	55
56	26,20	22,00	22,96	26,40	22,20	23,17	56
57	26,67	22,39	23,39	26,87	22,60	23,61	57
58	27,14	22,78	23,82	27,34	23,00	24,04	58
59	27,61	23,17	24,25	27,81	23,39	24,47	59
60	28,07	23,57	24,68	28,29	23,79	24,91	60
61	28,54	23,96	25,11	28,76	24,19	25,34	61
62	29,01	24,35	25,54	29,23	24,58	25,77	62
63	29,48	24,75	25,97	29,70	24,98	26,21	63
64	29,95	25,14	26,41	30,17	25,38	26,65	64
65	30,41	25,53	26,84	30,64	25,77	27,09	65
66	30,88	25,93	27,27	31,11	26,17	27,53	66
67	31,35	26,32	27,71	31,59	26,57	27,97	67
68	31,81	26,71	28,14	32,06	26,96	28,41	68
69	32,28	27,10	28,58	32,53	27,35	28,85	69
70	32,75	27,50	29,02	33,00	27,75	29,29	70
71	33,22	27,89	29,46	33,47	28,15	29,73	71
72	33,69	28,28	29,90	33,94	28,54	30,17	72
73	34,15	28,67	30,34	34,41	28,94	30,61	73
74	34,62	29,07	30,78	34,89	29,34	31,06	74
75	35,09	29,46	31,22	35,36	29,73	31,50	75
76	35,56	29,85	31,66	35,83	30,13	31,95	76
77	36,03	30,25	32,10	36,30	30,53	32,40	77
78	36,49	30,64	32,54	36,77	30,92	32,84	78
79	36,96	31,03	32,98	37,24	31,31	33,29	79
80	37,43	31,43	33,43	37,71	31,71	33,74	80

C ₁₅ H ₂₄ O				C ₁₅ H ₂₆ O			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
81	37,90	31,82	33,87	38,19	32,11	34,19	81
82	38,37	32,21	34,32	38,66	32,50	34,64	82
83	38,84	32,60	34,77	39,13	32,90	35,09	83
84	39,30	33,00	35,22	39,60	33,30	35,54	84
85	39,77	33,39	35,66	40,07	33,69	35,99	85
86	40,24	33,78	36,11	40,54	34,09	36,44	86
87	40,70	34,18	36,56	41,01	34,49	36,90	87
88	41,17	34,57	37,01	41,49	34,88	37,35	88
89	41,64	34,96	37,46	41,96	35,28	37,80	89
90	42,11	35,36	37,92	42,43	35,68	38,26	90
91	42,57	35,75	38,37	42,90	36,08	38,71	91
92	43,04	36,14	38,82	43,37	36,47	39,17	92
93	43,51	36,53	39,27	43,84	36,87	39,63	93
94	43,98	36,92	39,73	44,31	37,26	40,09	94
95	44,45	37,32	40,18	44,79	37,66	40,55	95
96	44,92	37,71	40,64	45,26	38,05	41,01	96
97	45,39	38,10	41,10	45,73	38,45	41,47	97
98	45,85	38,50	41,55	46,20	38,85	41,93	98
99	46,32	38,89	42,01	46,67	39,24	42,39	99
100	46,79	39,29	42,47	47,14	39,64	42,86	100
101	47,26	39,68	42,93	47,61	40,04	43,32	101
102	47,72	40,07	43,39	48,09	40,43	43,78	102
103	48,19	40,46	43,85	48,56	40,83	44,24	103
104	48,66	40,85	44,32	49,03	41,23	44,71	104
105	49,13	41,25	44,78	49,50	41,63	45,18	105
106	49,59	41,64	45,24	49,97	42,02	45,65	106
107	50,06	42,04	45,70	50,44	42,42	46,12	107
108	50,53	42,43	46,16	50,91	42,81	46,59	108
109	51,00	42,82	46,63	51,39	43,21	47,06	109
110	51,46	43,21	47,10	51,86	43,61	47,53	110
111	51,93	43,60	47,57	52,33	44,00	48,00	111
112	52,40	44,00	48,04	52,80	44,40	48,47	112
113	52,87	44,39	48,50	53,27	44,80	48,94	113
114	53,34	44,78	48,97	53,74	45,19	49,42	114
115	53,81	45,17	49,44	54,21	45,59	49,89	115
116	54,28	45,57	49,91	54,69	45,99	50,36	116
117	54,74	45,96	50,39	55,16	46,38	50,84	117
118	55,21	46,35	50,86	55,63	46,78	51,32	118
119	55,68	46,74	51,33	56,10	47,18	51,80	119
120	56,14	47,14	51,81	56,57	47,57	52,28	120

C ₁₅ H ₃₄ O				C ₁₅ H ₂₈ O			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
121	56,61	47,53	52,28	57,04	47,97	52,76	121
122	57,08	47,92	52,76	57,51	48,36	53,24	122
123	57,55	48,32	53,23	57,99	48,76	53,72	123
124	58,01	48,71	53,71	58,46	49,16	54,20	124
125	58,48	49,10	54,18	58,93	49,55	54,68	125
126	58,95	49,50	54,66	59,40	49,95	55,17	126
127	59,42	49,89	55,14	59,87	50,35	55,65	127
128	59,89	50,28	55,62	60,34	50,74	56,13	128
129	60,36	50,67	56,11	60,81	51,14	56,62	129
130	60,82	51,07	56,59	61,28	51,54	57,10	130
131	61,29	51,46	57,07	61,75	51,93	57,59	131
132	61,76	51,85	57,55	62,22	52,33	58,08	132
133	62,23	52,25	58,03	62,70	52,73	58,57	133
134	62,70	52,64	58,52	63,17	53,12	59,06	134
135	63,16	53,03	59,00	63,64	53,52	59,55	135
136	63,63	53,42	59,49	64,11	53,92	60,04	136
137	64,10	53,82	59,98	64,59	54,31	60,53	137
138	64,57	54,21	60,47	65,06	54,71	61,02	138
139	65,04	54,60	60,96	65,53	55,11	61,51	139
140	65,50	55,00	61,45	66,00	55,50	62,01	140
141	65,97	55,39	61,94	66,47	55,90	62,50	141
142	66,44	55,78	62,43	66,94	56,30	63,00	142
143	66,90	56,18	62,93	67,41	56,69	63,50	143
144	67,37	56,57	63,42	67,89	57,09	64,00	144
145	67,84	56,96	63,92	68,36	57,49	64,50	145
146	68,31	57,35	64,41	68,83	57,88	65,00	146
147	68,78	57,75	64,91	69,30	58,28	65,50	147
148	69,25	58,14	65,40	69,77	58,68	66,00	148
149	69,72	58,53	65,90	70,24	59,07	66,50	149
150	70,18	58,93	66,40	70,71	59,46	67,00	150
151	70,65	59,32	66,90	71,19	59,86	67,51	151
152	71,12	59,71	67,40	71,66	60,26	68,01	152
153	71,58	60,10	67,90	72,13	60,65	68,52	153
154	72,05	60,50	68,40	72,60	61,05	69,02	154
155	72,52	60,89	68,90	73,07	61,45	69,53	155
156	72,99	61,28	69,41	73,54	61,84	70,04	156
157	73,46	61,68	69,91	74,01	62,24	70,55	157
158	73,92	62,07	70,42	74,49	62,64	71,06	158
159	74,39	62,46	70,92	74,96	63,03	71,57	159
160	74,86	62,86	71,43	75,43	63,43	72,08	160

C ₁₅ H ₂₄ O				C ₁₅ H ₂₆ O			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
161	75,33	63,25	71,93	75,90	63,83	72,59	161
162	75,80	63,64	72,44	76,37	64,22	73,10	162
163	76,26	64,03	72,95	76,84	64,62	73,62	163
164	76,73	64,42	73,46	77,31	65,02	74,13	164
165	77,20	64,82	73,97	77,78	65,41	74,65	165
166	77,67	65,21	74,49	78,26	65,81	75,16	166
167	78,14	65,60	75,00	78,73	66,21	75,68	167
168	78,60	66,00	75,52	79,20	66,60	76,20	168
169	79,07	66,39	76,03	79,67	67,00	76,72	169
170	79,54	66,79	76,55	80,14	67,39	77,24	170
171	80,01	67,18	77,06	80,61	67,79	77,76	171
172	80,48	67,57	77,58	81,08	68,19	78,28	172
173	80,94	67,96	78,10	81,56	68,58	78,81	173
174	81,41	68,35	78,62	82,03	68,98	79,33	174
175	81,88	68,75	79,14	82,50	69,38	79,85	175
176	82,35	69,14	79,66	82,97	69,77	80,38	176
177	82,81	69,54	80,18	83,44	70,17	80,91	177
178	83,28	69,93	80,70	83,91	70,57	81,43	178
179	83,75	70,32	81,23	84,38	70,96	81,96	179
180	84,21	70,71	81,75	84,86	71,36	82,49	180
181	84,68	71,10	82,28	85,33	71,76	83,02	181
182	85,15	71,50	82,80	85,80	72,15	83,55	182
183	85,62	71,89	83,33	86,27	72,55	84,09	183
184	86,09	72,28	83,86	86,74	72,95	84,62	184
185	86,56	72,68	84,39	87,21	73,34	85,15	185
186	87,03	73,07	84,92	87,68	73,74	85,69	186
187	87,49	73,46	85,45	88,16	74,14	86,22	187
188	87,96	73,86	85,98	88,63	74,53	86,76	188
189	88,43	74,25	86,51	89,10	74,93	87,30	189
190	88,89	74,64	87,05	89,57	75,32	87,84	190
191	89,36	75,03	87,58	90,04	75,72	88,38	191
192	89,83	75,42	88,12	90,51	76,12	88,92	192
193	90,30	75,82	88,65	90,98	76,51	89,46	193
194	90,77	76,21	89,19	91,46	76,91	90,00	194
195	91,24	76,60	89,73	91,93	77,31	90,54	195
196	91,70	77,00	90,27	92,40	77,70	91,09	196
197	92,17	77,39	90,81	92,87	78,10	91,64	197
198	92,64	77,78	91,35	93,34	78,50	92,18	198
199	93,11	78,17	91,89	93,81	78,89	92,73	199
200	93,57	78,57	92,44	94,28	79,29	93,28	200

C ₁₅ H ₂₄ O				C ₁₅ H ₂₆ O			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
201	94,04	78,96	92,98	94,76	79,68	93,83	201
202	94,51	79,35	93,53	95,23	80,08	94,38	202
203	94,98	79,75	94,07	95,70	80,48	94,93	203
204	95,44	80,14	94,62	96,17	80,87	95,48	204
205	95,91	80,53	95,17	96,64	81,26	96,03	205
206	96,38	80,92	95,72	97,11	81,66	96,59	206
207	96,85	81,32	96,27	97,58	82,06	97,14	207
208	97,32	81,71	96,82	98,05	82,45	97,70	208
209	97,79	82,10	97,37	98,52	82,85	98,25	209
210	98,25	82,50	97,92	99,00	83,25	98,81	210
211	98,72	82,89	98,48	99,47	83,64	99,37	211
212	99,19	83,28	99,03	99,94	84,04	99,93	212
213	99,66	83,67	99,59	100,41	84,44	100,49	213
214	100,12	84,07	100,14				214

Geranyl tiglate: C₄H₇CO₂C₁₀H₁₇.

Ester number	% Ester	Ester number	% Ester	Ester number	% Ester	Ester number	% Ester	Ester number	% Ester
1	0,42	21	8,85	41	17,28	61	25,71	81	34,13
2	0,84	22	9,27	42	17,70	62	26,13	82	34,55
3	1,26	23	9,69	43	18,12	63	26,55	83	34,98
4	1,69	24	10,11	44	18,54	64	26,97	84	35,40
5	2,11	25	10,54	45	18,96	65	27,39	85	35,82
6	2,53	26	10,96	46	19,38	66	27,81	86	36,24
7	2,95	27	11,38	47	19,80	67	28,23	87	36,66
8	3,37	28	11,80	48	20,23	68	28,65	88	37,09
9	3,79	29	12,22	49	20,65	69	29,08	89	37,51
10	4,21	30	12,64	50	21,07	70	29,50	90	37,93
11	4,63	31	13,06	51	21,49	71	29,92	91	38,35
12	5,05	32	13,49	52	21,91	72	30,34	92	38,77
13	5,47	33	13,91	53	22,33	73	30,76	93	39,19
14	5,90	34	14,33	54	22,75	74	31,18	94	39,62
15	6,32	35	14,75	55	23,18	75	31,61	95	40,04
16	6,74	36	15,17	56	23,60	76	32,03	96	40,46
17	7,16	37	15,59	57	24,02	77	32,45	97	40,88
18	7,58	38	16,01	58	24,44	78	32,87	98	41,30
19	8,01	39	16,44	59	24,87	79	33,29	99	41,72
20	8,43	40	16,86	60	25,29	80	33,71	100	42,14



**From the Institute for Pharmacology and Physiological
Chemistry at Rostock i. M.**

Contributions

to

the knowledge of the pharmacological and physio-
logico-chemical behaviour of some volatile substances

by

Hans Kleist.

1. Anthranilic acid as a sodium salt.
2. Acetyl compound of methyl ester of anthranilic acid.
3. Methyl ester of methyl anthranilic acid as a sulphate salt.
4. Acetyl compound of methyl ester of methyl anthranilic acid.
5. Piperonal.

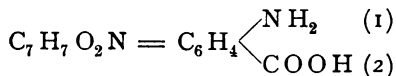
The number of plants containing volatile oils is enormous, and the variety of purposes for which these plants and their oils have been employed medicinally from time immemorial, in the most diverse countries, is also not inconsiderable. It should be the object of scientific pharmacology to ascertain to which constituents of the essential oils (which are mostly of very mixed compositions) the particular effects must be attributed. This question can only be solved in one way, and that a very difficult one; that is to say, by decomposing the oils into their constituents, and by testing each individual constituent for its physiologico-chemical and pharmacological behaviour. The decomposition of the oils is a subject to which a few individual chemists have applied themselves for many years, notably among them Wallach, and also Messrs. Schimmel & Co.; but the examination of the action of the constituents isolated from those oils is a long way behind. May the following pages form a small contribution towards the solution of this task.

I am indebted to the kindness of Professor Rudolf Kobert for having had placed at my disposal anthranilic acid and a few of its esters, and further piperonal, for the examination of their pharmacological properties, and of the fate of these bodies in the animal organism.

With the exception of piperonal, I have found in the literature on the subject no particulars on the physiologico-chemical and pharmacological behaviour of these substances.

Anthranilic acid and some of its esters.

Anthranilic acid



is orthoamido benzoic acid. Its melting point lies at 144° to 145° . The acid, which can be sublimed, is on distillation split up into aniline and CO_2 . In water and alcohol it is readily soluble; the aqueous solution shows a blue opalescence, and has a slightly sweet taste. Anthranilic acid crystallises in leaflets or trimetrical crystals. Salts of

platinum and gold are reduced already in the cold by anthranilic acid, also potassium permanganate; potassium chromate and bichromate, and salts of copper and silver, on the other hand, are not reduced even when the mixture is heated, the last-named salt not even when ammonia is added. If to an aqueous solution of anthranilic acid potassium ferricyanide and ferric chloride are added, a blue precipitate is formed. The sodium salt forms brownish-yellow laminæ which are very readily soluble in water. In an aqueous solution, when potassium-bismuth iodide is added, a yellow-red precipitate is formed.

Anthranilic acid is not apparently present in essential oils; but as derivatives of the acid are found in certain oils, it was necessary that a scientific investigation of these esters should be preceded by an examination of anthranilic acid itself.

For the experiments on animals sodium anthranilate was always selected.

Experiment No. 1. A frog weighing 44 g (for all the experiments with anthranilic acid and its esters the eatable frog, *Rana esculenta*, was employed) received 0,05 g sodium anthranilate dissolved in water. At the injection-spot the green and black pigment of the skin became almost immediately discoloured in a fairly sharply defined area of about 1 cm diameter; the skin assumed here a dirty yellow hue, which became tinged with red in consequence of the rapidly supervening hyperæmia. The passage of the sodium salt in the lymphatic vessel towards the zone of the pelvis was also marked by a slight discoloration of the pigment. In the course of the day the natural colours again became more pronounced, and after 24 hours the previously discoloured regions of the skin had again assumed their normal appearance. The same or corresponding symptoms after injection of sodium anthranilate, were subsequently not again observed, neither with the same frog, nor with others. For the rest, this dose of sodium salt had no apparent effect on the organism.

Experiment No. 2. The same frog was given 0,2 g sodium anthranilate. After 4 hours the animal felt very exhausted, and upon being stimulated mechanically, it crawled about slowly and with difficulty. The dorsal position was tolerated. After 5 hours, in the dorsal position, very slight tonic spasms, and slow irregular and inco-ordinated movements of the trunk, head, and extremities occurred. After 6 hours these inco-ordinated movements were only extremely feeble, the reflex-action scarcely noticeable. After 22 hours the animal was apparently dead, but by a small fenestra cut in the breast it was seen that the heart was still beating. After 44 hours the animal was found to be dead.

Experiment No. 3. A frog weighing 60 g, was given 0,1 g sodium anthranilate. No consequent symptoms were observed.

Experiment No. 4. A frog weighing 38 g received an injection of 0,15 g sodium anthranilate. After 5 hours the animal reacted little when stimulated; inco-ordinated and tonic movements were indicated. After 10 hours it was no longer possible to obtain reflex. Death supervened after about 40 hours. The section showed a medium degree of hyperæmia of the gastrointestinal tract, and of the mesentery. The mucous membrane of the mouth was not affected by the hyperæmia.

Experiment No. 5. 0,15 g sodium anthranilate was subcutaneously given to a frog weighing 45 g. After 3 hours the frog only made a few and futile efforts to change from the dorsal to the abdominal position. The movements

became increasingly feebler, the reflex had almost disappeared after $3\frac{1}{2}$ hours. At the trunk, but especially at the extremities, slight symptoms of stimulation occurred, which manifested themselves in faint inco-ordinated movements. Once there occurred even opisthotonos, lasting a few seconds. After 5 hours no reaction took place, and after 18 hours it was found that rigor mortis had set in.

Section: The stomach, which was in a highly hyperæmic condition, contained blood-stained mucus; the mesentery showed slight, the mucosa of the cavity of the mouth and of the gastro-intestinal canal but very little hyperæmia; the rectum alone was more strongly injected. The nerves and muscles reacted normally on electric stimulation.

Experiment No. 6. A frog weighing 50 g, which was in a somewhat enfeebled condition owing to previous experiments, received subcutaneously 0.1 g sodium anthranilate. After one hour the animal was already greatly exhausted. Death occurred after 4 hours.

Section: The mesentery was not hyperæmic. The alimentary canal, with the exception of the mucus membrane of the mouth, was slightly injected. The stomach contained blood-stained mucus.

Experiment No. 7. A medium-sized frog was given 0.1 g sodium anthranilate. No symptoms whatever occurred, not even the slightest.

Experiment No. 8. A frog weighing 58 g was injected on each of two consecutive days with 0.15 g sodium anthranilate, and on the third day with 0.2 g. The injections were also tolerated without consequent symptoms.

Experiments No. 9 and 10. One frog of 68 g received 0.2 g, and another of 60 g 0.15 g sodium anthranilate. No consequent symptoms whatever occurred.

Experiment No. 11. A frog weighing 69 g was given 0.4 g sodium anthranilate. After 4 hours isolated inco-ordinated movements were still observed; the reflex actions had completely disappeared, the action of the heart had become considerably slower. After $4\frac{3}{4}$ hours 0.00075 g nitrate of strychnine was injected. After 6 hours (i. e. $1\frac{1}{4}$ hours after the strychnine injection) convulsions and slight spasms of the extremities, of short duration, occurred on stimulation. No strychnine-action could be observed on the musculature of the trunk. After 18 hours the animal was found dead.

It follows from the foregoing that anthranilic acid paralyzes the central nervous system of the frog. The tonic spasms (which, however, were only slight) observed before the occurrence of absolute paralysis, are no doubt due to a less intense and transitory stimulation of the muscles or peripheral nerves. The ataxic movements, however, are probably due to the comparatively early paralysis of centripetal ducts, and the loss of controlling sensations thereby caused, with comparatively well-preserved motor-power. Strychnine in large doses, although it allows again a slight flicker of the reflex-action which had already disappeared, is not capable of completely removing the paralysing effect of anthranilic acid, or to prevent death. The fatal dose amounts to about 3.0 g per kilogram weight of the frog.

The urine of 24 hours of several frogs which had received an injection of anthranilic acid, was collected. After addition of potassium-bismuth iodide, a strong precipitate of a yellow-red colour was formed. The urine was now filtered, the residue on the filter collected, and decomposed with potash liquor;

it was then again filtered, and the filtrate exactly neutralised with sulphuric acid. After evaporating this neutral filtrate, it was repeatedly extracted with alcohol, the alcohol again driven off, and the small residue acidified with acetic acid, and precipitated with acetate of copper. In order to remove the copper from the liquid thus obtained, it was treated with sulphuretted hydrogen, and filtered. The filtrate had a faint yellowish colour, with a slight blue fluorescence. The melting point could not be determined, as the quantity remaining after slowly evaporating the water was too small. But the fluorescence could only have been caused by anthranilic acid.

If the fatal dose of anthranilic acid in frogs is not less than 3.0 g per kilogram, a more powerful toxic effect of the substance on warm-blooded animals may hardly be expected.

Experiment No. 12. A rabbit was injected with 1.0 g sodium anthranilate, without occurrence of any symptoms whatever. The quantity of urine obtained in 24 hours was 30 cc; it had an alkaline reaction, and contained neither sugar nor albumin. No aniline could be detected in the urine by means of chloride of lime. The urine was next added with alkali in order to test it for hippuric acid; it was evaporated to the consistency of syrup, the residue repeatedly extracted with cold alcohol, the alcoholic extract evaporated, decomposed with hydrochloric acid, and repeatedly shaken with acetic ether. In order to isolate benzoic acid, which possibly might be present, the residue, after driving off the acetic ether, was extracted with petroleum ether. But not even traces of benzoic acid could be detected. The residue from the acetic ether was dissolved in alcohol, when immediately a beautiful blue fluorescence appeared, which could only be due to the presence of anthranilic acid. One half of the solution was poured off, the alcohol evaporated, and the residue taken up with water. When potassium-bismuth iodide was added, a yellow-red precipitate was formed, but the pure anthranilic acid could not again be obtained.

In the remaining half of the alcoholic solution some crystals floated at the bottom of the vessel, which could only be dissolved with difficulty in cold alcohol, and not at all in ether. By means of ether they could very readily be freed from the greasy matter which still adhered to them. In hot water the crystals dissolved. After slowly evaporating the water, there could be detected with the microscope, firstly small rhombic prisms, secondly crystals arranged in druse-like form. The yield was too small for making any determinations whatever. Anorganic constituents were not present in the crystals.

Experiment No. 13. Even 5.0 g sodium anthranilate, injected subcutaneously in a medium-sized rabbit, had no effect. The urine collected in 48 hours had an alkaline reaction, and did not reduce a solution of copper with the application of heat. The fermentation test gave negative results. In about 15 cc urine submitted to the phenylglucosazone test, the precipitate contained only a few star-shaped crystals, quite isolated and badly formed, although the urine had been cooled very slowly on a water bath. They, however, proved that the urine contained traces of sugar.

Small traces of albumin could also be detected by means of Esbach's reagent, and the underlaying test with nitric acid.

The urine was rendered still somewhat more alkaline with soda, evaporated to the consistency of syrup, repeatedly extracted with alcohol, the alcohol extract evaporated, the residue decomposed with hydrochloric acid, and repeatedly shaken with acetic ether. The acetic ether showed intense fluorescence. As the fluorescence sufficed for the detection of anthranilic acid, the production of the acid in the pure state was not proceeded with. After driving off the acetic ether, the residue was taken up with water, rendered alkaline with soda, filtered, and acidified with an excess of hydrochloric acid. But no crystals as in the previous experiment could be obtained.

The residue of the evaporated urine was finally acidified with hydrochloric acid, once more evaporated, and treated with alcohol and acetic ether. The fluorescence of the latter was but very faint. This time also no crystals could be obtained.

Experiment No. 14. 2.0 g sodium anthranilate given subcutaneously to the same rabbit, caused no separation either of albumin or of sugar. The results of the examination of the urine were the same as in experiment No. 13.

Experiment No. 15. A medium-sized dog was treated subcutaneously with 2.0 g sodium anthranilate. No action. In the urine of 48 hours neither sugar nor albumin were present. The urine rendered alkaline with soda was evaporated to a syrupy consistency, and tested for hippuric acid. There remained a residue which only dissolved in cold water when soda liquor was added. After the solution had been acidified with an excess of hydrochloric acid, the substance was again precipitated. The residue collected from the filter after filtration was repeatedly purified in this manner. The substance has an acid character, and forms salts with bases; like hippuric acid, it dissolves with great difficulty in cold water and in ether, more readily in cold alcohol and acetic ether and hot water, and very rapidly in hot alcohol and hot acetic ether. The crystals of this acid wholly resemble those of hippuric acid, but it is not in this case a question of the last-named acid, whose melting point lies at 188° . The melting point of this acid lies between 315 and 318° . By means of potassium, potassium ferricyanide, and ferric chloride, the presence of nitrogen could be detected.

Experiment No. 16. The same dog received an injection of 4.0 g sodium anthranilate. The urine of 48 hours, which showed a slight fluorescence, had an alkaline reaction, contained no albumin, and reduced a solution of copper already in the cold. As this reduction in the cold could doubtless only have been caused by sugar, it was remarkable that the fermentation-test had a negative result. For purposes of control two fermentation tubes were now prepared with a solution of sugar of equal percentage. To one of these 0.05 g sodium anthranilate was added, and so much tartaric acid, that the liquid had a slightly acid reaction. After 6 hours the fermentation-process had in the one tube come to an end, whilst in the other tube, to which the substance had been added, no carbon dioxide had as yet evolved. Only after 24 hours a quantity of carbon dioxide had been formed which was less than half that in the other tube. Further fermentation did not, however, take place in the following 24 hours. Anthranilic acid or its salt, consequently, acts on the yeast, and retards, and therefore curtails, the process of fermentation considerably.

The presence of sugar in the urine was definitely proved by the phenylglucosazone test. Many and well-developed crystals of the characteristic form were obtained.

From the presence of sugar, and the negative result of the fermentation test, it may be concluded that the urine contained anthranilic acid, and that in such abundance, that it was capable of acting on the yeast.

The urine was now treated in the same manner as in experiment No. 13. The alcohol, and also the acetic ether, showed a beautiful blue fluorescence. But the acid which I obtained in experiment No. 15, could not be produced.

Experiment No. 17. A small dog, weighing about 16 pounds, was subcutaneously injected with 5.0 g sodium anthranilate. After 24 hours the animal was attacked by diarrhoea, and on the second day it took absolutely no food. On the third day it had completely recovered.

The urine collected in 48 hours was alkaline, showed a blue fluorescence, contained no albumin, and reduced solution of copper in the cold. The fermentation-test was negative; the phenylglucosazone-test yielded positive results.

In spite of the most careful examination (compare experiment No. 13) the acid obtained in the first experiment on the dog, could not now be produced.

Experiment No. 18. I personally took per os 2.0 g sodium anthranilate, viz., twice 1.0 g with an interval of 2 hours. Half an hour after each administration a slight attack of perspiration occurred without increase of temperature. About 3 hours after the last dose a slight but yet troublesome salivation was noticeable. Apart from a slight feeling of discomfort in the abdomen, which occurred 12 to 15 hours after administration, disturbances on the part of the gastro-intestinal canal remained absent. The stools were normal. The urine, collected in 48 hours, had an acid reaction; it showed an extremely intense fluorescence, contained no albumin, and reduced copper solution. The fermentation-test had negative, and the phenylglucosazone-test positive results. When soda was added, the fluorescence disappeared. No attempt was made to isolate anthranilic acid. No hippuric, benzoic, or any other organic acids whatever could be obtained from the urine which was treated in the same manner as described in experiment No. 13.

These experiments show that warm-blooded animals tolerate without lasting injury the injection, or administration per os, of anthranilic acid in considerable doses. In the worst case, diarrhoea and salivation occur. The substance is found back in the urine in an unchanged condition, and can already be recognized without chemical examination by the fluorescence. In addition to the substance, sugar is found in the urine of man and dog; in that of the rabbit, however, sugar is either not found at all, or, if very large doses have been given, only traces are present. The sugar can be detected either forthwith by means of the phenylglucosazone-test, or less readily by the fermentation-test, as our substance, like many other reducing bodies, impairs the fermenting power of the yeast.

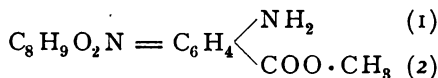
It was not possible to detect any action of anthranilic acid on bacteria.

One cc of a 3 per cent. solution of sodium anthranilate was added to cultures of each *Bacterium coli*, *Staphylococcus albus* and *Bacillus subtilis*, which had been inoculated in about 4 cc peptone-water. When the substance had been in contact with the bacteria for 48 hours at a constant temperature of 34°, the cultures were inoculated into alkaline peptone-agar. Their growth was vigorous and showed no difference from that of control-cultures which had not been treated with anthranilic acid. It follows that sodium anthranilate, in a 0.06 per cent. solution, during 48 hours' action, does not exert any demonstrable influence on *Bacterium coli*, *Staphylococcus albus*, and *Bacillus subtilis*.

It was also impossible to prove any influence of the sodium salt of anthranilic acid on hæmachrome and on the red blood corpuscles.

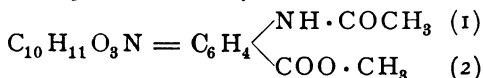
Acetyl compound of methyl ester of anthranilic acid.

Methyl ester of anthranilic acid



was discovered in the year 1894, in the laboratory of Messrs. Schimmel & Co., as a constituent of oil of orange flowers (neroli oil). It plays an important part in the formation of the aroma of the orange-flower. The proportion of methyl anthranilate in oil of orange-flowers is about 0,6 per cent. The melting point of this compound lies at 25,5°. The solutions show a beautiful blue fluorescence. In the undiluted state the full odour is disagreeable, and only when it has been diluted in due proportion, it reminds of the odour of orange flowers. When a solution of methyl ester of anthranilic acid in water is submitted to distillation, the ester passes over into the receiver. The ester has basic properties.

The acetyl compound of methyl ester of anthranilic acid:



represents a loose flocculent white powder free from odour and taste, which can be sublimed. In cold or hot water it dissolves with difficulty; in alcohol, ether, and concentrated hydrochloric acid it is readily soluble. Its solutions show no fluorescence. From water the acetyl compound crystallises in delicate needles. It does not reduce solutions of salts of copper, silver, gold or platinum, or of potassium chromate and permanganate. With platinum chloride it forms a double salt, which crystallises out in beautiful, long needles. When boiled for several hours in concentrated hydrochloric acid, it splits up into methyl anthranilate and acetic acid.

The physiological action of the acetyl compound of methyl ester of anthranilic acid on the animal organism is also slight.

Experiment No. 1. A frog weighing 52 g received 0,1 g methyl ester of acetyl anthranilic acid in emulsion with olive oil. After 45 minutes the animal in dorsal position (without being able to turn over on its abdomen) still made fairly strong movements as if swimming, but subsequently only a few inco-ordinate movements. After 1½ hours the frog lay quietly; the reflex-action was much reduced, and after 4 hours only indicated. The heart continued its normal action for several hours longer. After 18 hours the frog was found dead.

Section: The cavity of the mouth slightly injected. The stomach was filled with a glutinous green mucus; the intestine also contained some greenish mucus. The stomach and mesentery were strongly injected; the intestine had a dark-red appearance, in consequence of hyperæmia. No blood extravasation was present in the alimentary tract. When stimulated electrically, the muscles and nerves reacted normally.

Experiment No. 2. A frog of 40 g weight received 0.05 g methyl ester of acetyl anthranilic acid in emulsion with olive oil. Only after 2 hours the dorsal position was tolerated, and the reflex-actions commenced to grow more feeble. After 18 hours reflex-action could no longer be produced. The heart beat slowly and faintly. After 28 hours, on stimulation, the first faint reflex-actions again became noticeable; in the course of the day they grew stronger. After 3 times 24 hours the frog had so far recovered that it no longer tolerated the dorsal position.

Experiment No. 3. A frog weighing 28 g (which appeared to be somewhat exhausted already before the experiment) received a subcutaneous injection of 0.04 g of the acetyl compound. After $\frac{3}{4}$ hour the dorsal position was tolerated without the slightest resisting movements. The reflex-action was still good, but disappeared completely already after $2\frac{1}{2}$ hours. The action of the heart after 16 hours was scarcely perceptible. Death occurred after about 70 hours.

Section: Cavity of the mouth, and also the mesentery, moderately injected. The stomach and intestine were strongly hyperæmic, but without extravasation of blood.

Experiment No. 4. A frog weighing 30 g received an injection of 0.04 g methyl ester of acetyl anthranilic acid. An hour later the frog was still perfectly healthy, but after 2 hours it was no longer able to turn over on the abdomen. The reflex-action even after $3\frac{3}{4}$ hours was still normal. In the dorsal position some faint swimming movements were made. Respiration was superficial, but had not become slower. The reflex-action gradually decreased, and ceased after 38 hours. Death occurred after 4×24 hours.

Section: The cavity of the mouth, and the stomach and intestine, were slightly injected. A completely-filled galleyst of 1.4 cm diameter, whose walls were also slightly injected, was situated on the liver.

Experiment No. 5. A frog weighing 31 g was injected with 0.02 g of the acetyl compound. After 45 minutes the animal felt somewhat feeble, and after $2\frac{1}{2}$ hours no longer resisted the dorsal position. In that position it made some inco-ordinate movements. Slight swimming movements in the dorsal position were made after $3\frac{3}{4}$ hours. At this time the respiration became slower and more superficial, but it became again normal after 21 hours. Recovery progressed but slowly. After 3×24 hours the frog was found in a sitting posture, and appeared to be healthy, but, when placed in the dorsal position, it could not turn over on its abdomen in spite of all efforts. During the whole time the action of the heart had remained good, and the reflex-action had not diminished.

Experiment No. 6. The same dose was given to a frog of 27 g weight. After 45 minutes it could only turn over with difficulty from the dorsal to the abdominal position. Reflex-action had disappeared already after 2 hours. The action of the heart which grew increasingly feeble, again became stronger after 18 hours. When stimulated, a slight reaction also became again noticeable. After 3×24 hours the frog, like the one in experiment No. 5, appeared to be in a healthy state when in the abdominal position. When turned on its back, it suddenly breathed very rapidly and deeply. The extremities, especially those in front, thereby showed slight clonic and tonic spasms. A complete recovery only occurred after 4×24 hours (from the time of injection).

Experiment No. 7. A frog weighing 42 g received a dose of 0.1 g of the substance. When after $\frac{3}{4}$ hour the reflex-action had ceased, it made some isolated inco-ordinate movements. After 18 hours it was found dead.

Experiment No. 8. The same dose was given to a frog weighing 63 g. 45 minutes later, when it was absolutely without reaction, an injection was made with 0.0006 g strychnine nitrate. The action of the strychnine became

apparent after 30 minutes by slight twitchings after stimulation. Tetanus did not occur. When 5 hours after the first injection (i. e. of the acetyl compound) the action of the strychnine had again almost disappeared, another injection was made with 0.000025 g strychnine. After this injection also only convulsions occurred, but no tetanus. 18 hours after injection of the ester the frog was found dead.

It appears from these experiments, that the action of the acetyl compound of methyl ester of anthranilic acid is similar to that of anthranilic acid. After a few inco-ordinate movements, paralysis of the central nervous system occurs, which is not completely removed even by large doses of strychnine. The fatal dose, of which the quantity does not appear to be affected by strychnine, amounts to about 1.0 g per kilogram weight of the frog.

While the frogs were being dissected (experiments No. 1, 3 and 4), an intense and penetrating odour of orange flowers was emitted from the portions of the body. The urine of the frogs which survived the injection, possessed the same characteristic aromatic odour. From the ether, with which a few cc urine of the frogs was repeatedly extracted, no crystals of methyl ester of acetyl anthranilic acid could be obtained. The compound consequently is split up completely in the organism of the frog into acetic acid and methyl anthranilate, the presence of which is revealed by its peculiar aromatic odour.

Experiments No. 9 and 10. On rabbits and dogs (of medium size) doses of 1.0 g methyl ester of acetyl anthranilic acid, in oil emulsion, had no effect. Sugar and albumin were not detected in the urine. On account of the strong odour proper to the urine, an aromatic odour like orange-flowers could not be determined with certainty.

As methyl ester of anthranilic acid, as a primary aromatic base, forms azo-dyes, this property can be made use of for purposes of demonstration. The dye has a yellow-red colour, is insoluble in water, but dissolves in concentrated sulphuric acid with a deep violet colour. The insolubility of the dye in water permits a quantitative estimation of methyl ester of anthranilic acid in solutions and in essential oils. For this purpose a definite quantity of the diazotised solution of methyl ester of anthranilic acid is titrated with an alkaline solution of β -naphthol, when the dye thereby produced is precipitated. The litmus test shows whether the reaction is completed.

In accordance with Erdmann's method [comp. Berliner Berichte 35 (1902) 24] 0.5 g β -naphthol, purified by crystallisation from hot water, was dissolved in 0.5 cc soda liquor and 150 cc water with the addition of 15 g sodium carbonate.

A portion of the urine obtained from the rabbits was acidified with hydrochloric acid, and diazotised at a low temperature with a 5 per cent. solution of nitrite. When, after a few minutes, free nitrous acid could be detected by means of potassium iodide and starch paper, a measured quantity of the β -naphthol solution was titrated with this urine. After a few minutes a dark-red colouring-matter appeared, which, however, was not precipitated, but, on the contrary, dissolved immediately. It is quite possible that the solubility of the azo-dye was due to the presence of ammonia. Although this method therefore

also proved useless for the quantitative estimation of methyl ester of anthranilic acid, it had yet demonstrated, that the acetyl compound is not again separated out as such, but, on the contrary, in the animal organism passes over into the methyl ester, with loss of the acetyl-group.

The other portion of the urine of the rabbits was slightly acidified with hydrochloric acid, carefully and slowly evaporated to the consistency of syrup, extracted with alcohol, the alcohol again driven off, and the residue dissolved in a few drops concentrated hydrochloric acid and a small quantity of water. After adding alcohol, small crystals, glittering in the liquid, were precipitated. Examined under the microscope, they were found to be small lancet-shaped laminae, of which the majority possessed a fine serrated edge. As soon as the solution was heated, the crystals dissolved again. It was probably a question of hydrochloric methyl ester of anthranilic acid, which was precipitated from the aqueous solution when alcohol was added. After again slowly evaporating the alcohol and water, a white mass remained which was interspersed with greasy constituents. These could be readily removed from the white salt by means of alcohol. The presence of free methyl ester of anthranilic acid could be recognised by a slight blue fluorescence of the alcohol. The residue was dissolved in a weak solution of soda, and extracted with ether. The ether showed a strong blue fluorescence. After driving off the ether, there remained no crystals of the acetyl compound, but a thin oily film with an offensive odour was found to adhere to the glass. The small contents of the vessel were washed out with 1 to 2 cc dilute hydrochloric acid, and diazotised with sodium nitrite, and with this solution a solution of β -naphthol was titrated. As was to be expected, the azo-dye was now obtained insoluble.

With the urine of the dogs the diazo-reaction also gave positive results. But, as in the case of the urine from rabbits, the dye immediately dissolved. A portion of the urine was submitted to distillation. The distillate in the receiver had an extremely strong ammonia-like odour. As in the distillation of a solution of methyl ester of anthranilic acid the ester also passes over into the receiver, it was clear that in the distillate of the dog's urine it should be possible to detect methyl ester. And as a matter of fact, in the diazo-test the same red dye occurred again, which immediately dissolved in the liquid.

The other portion of the urine of the dog was acidified with sulphuric acid, evaporated to one-fourth its volume, next rendered again strongly alkaline with soda liquor, and a few times extracted with ether. The ether showed a strong blue fluorescence. Crystals of methyl ester of acetyl anthranilic acid could not be obtained from the ether; that is to say, the acetyl compound had been completely decomposed.

It follows that doses of 1.0g of the acetyl compound of methyl ester of anthranilic acid are tolerated by rabbits and dogs without any apparent or demonstrable disturbance. The acetyl-group is completely split off in the animal organism, and the methyl ester of anthranilic acid can be detected in the urine by means of the diazo-reaction after having been isolated by extraction with alcohol.

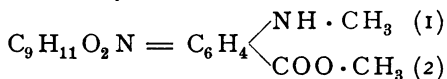
On bacteria the acetyl compound had no influence, as was shown by experiments carried out in the same manner as with sodium anthranilate (compare page 116). The developing capacity of *Bacterium coli*, *Staphylococcus albus* and *Bacillus*

subtilis, was in no way impaired after 48 hours' action of a 0,8 per cent solution of the substance.

The acetyl compound also exerts does not act hæmachrome and red blood corpuscles.

Methyl ester of methyl anthranilic acid.

Methyl ester of methyl anthranilic acid:



is an oily liquid with a sweetish, penetrating, aromatic odour which to some extent reminds of the odour of oranges. This ester, whose melting point lies between 18,5° and 19,5°, occurs regularly in oil of mandarins, and also (as has recently been determined in the laboratory of Messrs. Schimmel & Co.) in oil of rue. In water it is only sparingly soluble, but in alcohol and ether it dissolves in every proportion. Its solutions also show a magnificent blue fluorescence. As it possesses basic properties, it forms salts with acids. The preparation placed at my disposal was the sulphate of methyl ester of methyl anthranilic acid. It is readily soluble in water, but is then for the greater part decomposed into free sulphuric acid and methyl ester of methyl anthranilic acid. For this reason the essential oil floats on the fluorescent water which turns litmus paper red. After adding soda liquor, the sulphuric acid combined with the dissolved ester salt is now also abstracted from the latter, and the oil which is then finely divided in the water, gives it a milky appearance.

Solutions of gold, silver and platinum are reduced by the ester salt, but not copper solution. Potassium chromate and bichromate are only reduced in the acid solution of the salt.

When potassium permanganate is added to an aqueous solution of sulphate, there appears at first a yellow-green hue, which almost immediately changes into deep blue-black. After a few minutes this colour also disappears, to make room for a delicate bright-red hue. This red solution has at first an intense dirty slaty-blue fluorescence, but after a few hours this appearance vanishes completely. While gradually manganese dioxide is precipitated and deposited at the bottom, the liquid acquires a reddish-brown shade.

If a sulphate solution is selected which has been neutralised or rendered alkaline with soda, there occurs, after potassium permanganate is added, only a green hue, and after a few hours manganese dioxide is precipitated whilst the liquid acquires a dirty turbidity.

With potassium ferricyanide and ferric chloride, the sulphate (and consequently methyl ester of methyl anthranilic acid) forms a blue

precipitate. This reaction is so delicate that even in 0,000000000001
 $= \frac{1}{10^{12}}$ g of the sulphate, methyl ester of methyl anthranilic acid could be detected.

When mercuric iodide is added to a sulphate solution, no precipitate is formed. But after prolonged standing bright-yellow prisms crystallise out. Of some few of these prisms the angles are truncated.

With potassium-bismuth iodide the sulphate forms a red precipitate, from which in a few days magnificent red prisms separate out.

In an acid and highly concentrated solution of the salt, a white, delicately violet-coloured precipitate is formed when phosphotungstic acid is added.

If to a sulphate solution a concentrated solution of iodine and potassium iodide, or the so-called Florence-solution, be added, a thick, brown precipitate is formed; this precipitate, after several hours, crystallises out in the form of brown, sharp needles, which arrange themselves in the form of stars or in druse-form. These also form a blue precipitate with red prussiate of potassium and ferric chloride.

The physiological effect of methyl ester of methyl anthranilic acid in the animal organism is unimportant, like that of the other substances already discussed.

For the following experiments, an aqueous and exactly neutralised solution of the sulphate was always selected.

Experiment No. 1. A large strong frog received a subcutaneous injection of 0,05 g of the salt. The animal gradually became more and more feeble; after 1½ hours, it made at first only faint and fruitless efforts to change from the dorsal to the abdominal position, but subsequently, when in the dorsal position, it made powerful swimming movements with the hind legs. The reflex-action was scarcely diminished; respiration and action of the heart were not impaired. After 4 hours the first symptoms of recovery became apparent.

Experiment No. 2. The same frog, after 24 hours, when it had completely recovered, received 0,075 g. The same action was observed.

Experiment No. 3. A frog weighing 52 g received 0,07 g. After an hour the animal was already very weak. The reflex-action of the anterior extremities ceased after 2 hours, that of the hind legs had slightly diminished. The action of the heart remained constantly good. After 20 hours the animal had recovered.

Experiment No. 4. A frog weighing 65 g received 0,075 g. After one hour feebleness occurred which increased up to the third hour. At this time slight disturbances of the co-ordination were also observed. For the rest, the symptoms and the course were the same as in experiment No. 1.

Experiment No. 5. The same frog, two hours after an injection of 0,1 g, was very exhausted; the reflex-action diminished more and more, was only very feeble after 2½ hours, and had completely ceased after 16 hours. Not until after 43 hours some slight reflex-action of the extremities could again be excited by stimulation. The action of the heart had throughout this time remained good and strong. After 54 hours the animal had recovered.

Experiment No. 6. A frog weighing 26 g received 0,15 g of the substance. After 10 minutes the animal had already ceased to react, and the action of the heart could no longer be observed. After 9 hours rigor mortis had set in.

Section: The skin was normal, the cavity of the mouth slightly red; the stomach, which contained a glutinous, glassy mucus, was strongly injected. The other organs were in no way abnormal. The nerves and muscles responded normally to electric stimulation.

Experiment No. 7. A frog weighing 45 g received a dose of 0,2 g. The animal, which ceased to react already after a few minutes, was injected after 15 minutes with 0,00005 g strychnine nitrate. This only caused convulsive movements, but no tetanus. The action of the heart still continued for a comparatively long time, although it was scarcely perceptible. After 20 hours the animal was found dead and rigid.

The section gave the same results as in experiment No. 6.

Methyl ester of methyl anthranilic acid administered to frogs paralyses the central nervous system, and its toxic action is not appreciably influenced by strychnine. The fatal dose of the sulphate of the ester is about 4,0 g per kilogram weight of the frog.

Experiments Nos. 8 and 9. Doses of 0,5 g and 1,4 g of sulphate of methyl ester of methyl anthranilic acid (subcutaneously) had no perceptible effect to rabbits.

Experiment No. 10. A medium-sized dog also tolerated 2,1 g very well.

It should be mentioned, however, that both in the dog and in the rabbit, during the 24 hours after injection, slight catarrhal symptoms of the superior respiratory passages occurred.

The urine of both the rabbit and the dog contained neither albumin nor sugar.

The urine of the rabbit, which possessed the aromatic odour of methyl ester of methyl anthranilic acid, after having been acidified with sulphuric acid, was reduced to about one fourth its volume, then rendered decidedly alkaline by soda liquor, and extracted with ether. The ether showed an intense blue fluorescence. After adding a few cc water, the ether was slowly driven off. There remained on the water numerous small drops of oil coloured brown-black by dirty matter. Attempts to remove the adhering dirt from the oil drops did not succeed. With potassium ferricyanide and ferric chloride the drops formed a strong blue precipitate. As soon as a few drops concentrated sulphuric acid were added to the water, the oil dissolved in the latter. In the presence of Florence-solution a brown precipitate was formed, which changed into crystals of druse-like formation. A solution of potassium permanganate was quickly discoloured, without the occurrence of the previously described hues.

The aromatic odour of methyl ester of methyl anthranilic acid in the urine of rabbits; the fluorescence of the ether; the intense Berlin-blue reaction of the oil drops; the precipitate and the crystals from the Florence-solution; the difficult solubility of the oil in the presence of acids; all these facts prove that it can only have been a question of methyl ester of methyl anthranilic acid. The fact that potassium permanganate was discoloured without the occurrence of those hues, was possibly due to contamination of the ester.

From the urine of the dog the oil-drops could also be obtained in the same manner. They showed the same behaviour.

Finally, in the urine of the frogs the presence of the ester could be demonstrated by means of iron. The urine was strongly shaken with ether. After driving off the latter, and treating the scarcely visible fatty residue with potassium ferricyanide and ferric chloride, the blue colouring matter was precipitated.

It follows from the foregoing that methyl ester of methyl anthranilic acid is tolerated by warm-blooded animals in comparatively large doses without injurious effect, and without the occurrence of any apparent disturbances in the organism whatever.

The substance therefore again passes out of the animal organism as such. But the ester is separated out not only by the kidneys, but also by the superior respiratory passages. This conclusion at least is justified by the catarrhal symptoms occurring in the dog and the rabbit after the injections.

In spite of its low physiological action, methyl ester of methyl anthranilic acid possesses the properties of a bactericide.

The experiments with this substance made for the purpose of determining the intensity of the action on bacteria, were carried out in this manner, that to a measured quantity of peptone-water into which the bacteria had been inoculated, 24 hours after the inoculation was added one cc of an aqueous solution containing a definite percentage of the sulphate of methyl ester of methyl anthranilic acid.

When the ester had acted for 24 hours, the micro-organisms were again inoculated into alkaline peptone-agar. The temperature of the incubator in which the bacteria were placed, was kept throughout at 34°.

The aqueous solutions of the ester were freshly prepared for each experiment, and not only acid solutions were employed, but also such which had been exactly neutralised by soda. This was done not so much with the view of removing the small quantity of free sulphuric acid (which, as a matter of fact, could not exert any influence on the bacteria selected), as for this reason, that possibly the action of pure methyl ester of methyl anthranilic acid might differ from that of the ester combined with sulphuric acid.

The experiments were made at first with *Bacterium coli*, *Staphylococcus albus* and *Bacillus subtilis*. But as the development of the last-named was not retarded even in a 0,15 per cent. solution of the ester, only the two first-named micro-organisms were employed in the subsequent experiments. The results, which were frequently checked, are given in the following tables.

Bacterium coli.

In acid solution of the sulphate of methyl ester of methyl anthranilic acid.		In solution of sulphate of methyl ester of methyl anthranilic acid, rendered alkaline with soda.		
After 24 hours' action of the solution on the bacteria, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were:		The percentage of the substance in the solution acting on the cultures was:	After 24 hours' action of the solution on the bacteria, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were:	
sterile	} and remained so.	0,08 %	sterile	} and remained so.
sterile		0,06 %	sterile	
sterile		0,05 %	sterile	
found to contain from 1 to 4 small colonies.		0,04 %	found to contain sparsely developed colonies.	
found to contain sparsely and badly developed colonies.		0,03 %	crowded with well - developed colonies.	
crowded with well - developed colonies.		0,02 %		

Staphylococcus albus.

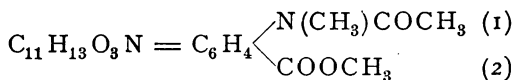
In acid solution of the sulphate of methyl ester of methyl anthranilic acid.		In solution of sulphate of methyl ester of methyl anthranilic acid, rendered alkaline with soda.	
After 24 hours' action of the solution on the cocci, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were:		The percentage of the substance in the solution acting on the cultures was:	After 24 hours' action of the solution on the cocci, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were:
sterile	} and remained so.	0,1 %	crowded with strongly-developed colonies.
sterile		0,08 %	do.
sterile		0,06 %	do.
found to contain strongly-developed colonies.		0,05 %	do.

These two tables do not show any pronounced difference in the results. The bactericidal action of methyl ester of methyl anthranilic acid within 24 hours asserts itself in the case of *Bacterium coli* already in a 0,05 per cent., and in that of *Staphylococcus albus* in a 0,06 per cent. solution of the sulphate, whilst the action of the solutions which have been neutralised with soda is less powerful. This difference in the action of the two solutions is not very great in the case of *Bacterium coli*, but yet noticeable; in that of *Staphylococcus albus*, however, it is very marked. In order to destroy this micro-organism in 24 hours, a 0,06 per cent. acid solution, or a neutralised solution of 0,15 per cent. is required. It would appear that the free sulphuric acid, which in such dilution as in these experiments does not impair or weaken, but rather favours the development both of *Bacterium coli* and of *Staphylococcus albus*, in the presence of the ester still enhances the bactericidal effect of the latter.

Hæmachrome and red blood corpuscles are not attacked either by methyl ester of methyl anthranilic acid, or by a neutralised solution of its sulphate. But an acid sulphate solution immediately causes the formation of methæmoglobin, with lixiviation of the red blood corpuscles, an action which of course does not result from the presence of the ester, but from that of the sulphuric acid.

Acetyl compound of methyl ester of methyl anthranilic acid.

The acetyl compound of methyl ester of methyl anthranilic acid



is a yellow oily substance, which has a bitter and slightly pungent taste, and which solidifies at 15° . In the undiluted state this body has a faint, offensive odour, and only when it is strongly diluted it acquires a penetrating aromatic sweetish odour which distantly reminds of the odour of orange-flowers. In alcohol, ether, and water the oil is soluble in every proportion. The substance shows no fluorescence.

It does not reduce solutions of copper, nor of gold, platinum, silver, potassium chromate, and potassium permanganate.

When Florence-solution is added to an aqueous solution of this substance, a brown precipitate is formed, which after several hours crystallises out in the form of hexagonal light-brown laminæ and

rhombic prisms. In transmitted light the prisms are partly light-brown, partly black coloured.

If to an aqueous solution of methyl ester of acetyl methyl anthranilic acid, after the addition of Florence-solution, soda liquor is added, the precipitate dissolves with a bright-yellow colour, and is not formed again even when an excess of hydrochloric acid is added. On the other hand, there is formed, either immediately, or, in case of insufficient concentration, in the course of 24 hours, an abundant precipitate of delicate sharp needles, which in transmitted light have a greenish-blue, and in reflected light a green-black colour. In hot water and in dilute soda liquor they dissolve immediately, but are again precipitated after the addition of hydrochloric acid.

With potassium ferricyanide and ferric chloride the acetyl compound does not form a blue precipitate.

A short time ago the makers succeeded in producing the acetyl compound of methyl ester of methyl anthranilic acid in crystalline form, instead of the amorphous mass hitherto obtained. The preparation placed at my disposal consisted of small crystals, which liquefied into an oil on being slightly heated. Treated with Florence-solution they formed a precipitate only when a small quantity of hydrochloric acid was added, but this precipitate did not crystallise out. After adding soda and hydrochloric acid the above-mentioned crystalline needles were precipitated.

For the following experiments on animals with the acetyl compound of methyl ester of methyl anthranilic acid, the form in which the compound was used was always that of aqueous solutions of the first consignment, except in those cases where the remarks show that either the pure substance was employed, or else aqueous solutions of the second consignment.

Experiment No. 1. A frog weighing 53 g received 0,0458 g. After 25 minutes it reacted but little. The action of the heart remained good. After 18 hours the frog was found to be again quite healthy.

Experiment No. 2. A frog weighing 60 g received 0,06 g. After 30 minutes the reflex-action was only feeble. Complete absence of reaction was observed after 4 hours, but the heart acted powerfully. After 24 hours the animal had made fair progress towards recovery.

Experiment No. 3. A frog weighing 60 g, 15 minutes after injection of 0,09 g, tolerated already the dorsal position; reflex-action was only faintly indicated, and ceased completely shortly afterwards. The action of the heart diminished gradually, and was subsequently hardly perceptible. The first slight reflex-action was again obtained after three times 24 hours; it increased a little in the course of the fourth day, but had again ceased after 104 hours (after injection). On the abdomen, and especially on the lower part of the throat and mouth, and also on the axillary and inguinal regions, and the lower part of the upper thigh, there appeared on the third day a few papillæ varying in size from that of a poppy-seed to a millet-grain, and having a reddish-yellow colour. After five times 24 hours the frog was found dead, but not rigid.

Section: The abdominal wall, stomach and intestine were strongly injected. The injected condition of the intestine diminished towards the cloaca.

A portion of the skin on which the papillæ were situated, after being hardened, was placed in paraffin, and stained. When examined under the microscope, it was found that at the places where the papillæ were situated, the layer of epithelium was raised. The contents of these vesicles consisted of a few detached epithelial cells which were partly already without nucleus, and a small quantity of detritus. At a few isolated parts of the skin which under the microscope did not externally show any change, the epithelium was also already raised.

Experiment No. 4. A middle-sized frog received the same dose. After one hour the animal was absolutely without reaction. Death occurred after about 36 hours.

The section showed the same results as in experiment No. 3, except that the abdominal wall was not hyperæmic.

Experiment No. 5. A medium-sized frog received 0,1 g. After $\frac{1}{2}$ hour the animal had lost all power of reaction; the action of the heart had diminished and become slower. After 24 hours the frog was found dead.

Section: The intestine showed general hyperæmia especially well-marked in certain circumscribed spots. The stomach which was also in a strongly injected condition, contained blood-stained mucus. The skin showed no peculiarities.

When the undiluted substance was injected, it acted already after a few minutes.

Experiment No. 6. A frog weighing 25 g received an injection of 0,14 g of the methyl ester of acetyl methyl anthranilic acid which I had received with the second consignment. After 10 minutes the animal had ceased to react. On electric stimulation the muscles and nerves reacted in a normal manner. The action of the heart was slow and feeble. After 15 minutes an injection was made of 0,00005 g strychnine nitrate; this produced no convulsions, but only slight twitching in response to stimulation. After 20 hours the frog was found rigid.

Section: The skin was normal, the cavity of the mouth slightly red; the stomach and intestine were strongly hyperæmic. The latter contained blood-stained mucus in addition to fæcal matter.

It must appear remarkable that in other frogs the formation of vesicles on the skin did not occur, either when smaller doses were given than in experiment No. 3, or in the case of equal or larger doses; and that, in fact, the abdominal wall of those animals was not even hyperæmic. At first the view was not wholly unwarranted, that possibly, in consequence of secretion of the substance through the skin, irritation of the latter by the essential oil might have occurred, followed by the formation of vesicles. This view, however, had to be abandoned, when it was subsequently found that the acetyl-group is split off in the body of the frog, and only the methyl ester of methyl anthranilic acid is excreted. But the same action on the skin was not observed in the case of methyl ester of methyl anthranilic acid (compare page 122).

Moreover, I do not believe that the acetyl compound alone is capable of producing such comparatively powerful changes, without acting in an equally strong manner in the interior of the organism,

especially on the intestine and stomach. The occurrence of the vesicles on the side of the abdomen rather points to some external local cause.

The frog survived by $3\frac{1}{2}$ days the one (experiment No. 4) which had received the same dose of 0,09 g, and by 4 days the other one (experiment No. 5) which had received 0,1 g. The action, therefore, was considerably less powerful. It is probable that shortly after the injection a few drops of the acetyl compound had again flown out of the puncture canal, and as the plate on which the frog was placed, was not kept very damp, those drops could exert a caustic action on the abdomen of the animal.

The acetyl compound of methyl ester of methyl anthranilic acid, like the other substances already discussed, paralyzes the central nervous system of the frog, but this toxic effect occurs comparatively rapidly, in any case at a considerably earlier period than with the other substances. Strychnine administered after poisoning with the acetyl compound, also induces a slight revival of the extinguished reflex-actions, but for the rest does not possess any antidotal properties. The fatal dose of the acetyl compound of methyl ester of methyl anthranilic acid amounts to 1,5 g per kilogram weight of the frog.

Before discussing the examination of the urine of the frogs, I will deal with the experiments made with this acetyl compound on warm-blooded animals.

Experiment No. 7. A guinea pig, weighing 500 g, received 0,55 g subcutaneously. After a few minutes it made some ataxic movements, fell down on its side, and fell asleep. The reflexes of the hind legs were much reduced, and had completely disappeared after 3 hours; those of the anterior extremities still remained indicated for a long time. Occasionally the animal, in the dorsal position, spontaneously made some slow walking-movements with the front legs; at the hind legs there occurred only short single twitches at intervals of from 1 to 15 minutes. The respiration gradually became slower and very superficial; the frequency of the pulsations of the heart also became reduced, but the energy of the contractions, as far as it could be judged after the puncture was made, still remained normal. After $5\frac{1}{2}$ hours the corneal-reflex also ceased. During somnolence about 2 cc alkaline, milky urine could be pressed out of the bladder. After 19 hours the animal was found dead and rigid.

Section: At the injection-spot a briny oedema had occurred. Hyperæmia could not be detected in any of the organs. The intestine was moderately filled with formed faecal matter. Kidneys, liver, lung and heart showed no peculiarities.

Experiment No. 8. A small rabbit received subcutaneously 0,5 cc of the undiluted acetyl compound of methyl ester of methyl anthranilic acid. After a few minutes it made inco-ordinate movements, fell down, and fell asleep. The power of reaction of the hind legs was much reduced. Respiration and pulsation were neither slower nor more feeble. After lying down for half an

hour, it turned over a few times as if about to wake up. In the course of 5 hours it had completely recovered, and took food.

Experiment No. 9. A full-grown medium-sized rabbit received 0.55 g subcutaneously. The animal soon became feeble, and after half an hour sat down quietly. When laid on the back, it regained its feet only slowly. The reflex-actions, respiration, and pulsation were not reduced. After 3 hours it had recovered fairly well.

This rabbit died suddenly 5 weeks afterwards. The internal organs, with the exception of the stomach, were found to be normal. But at the pylorus several ulcers were found, varying in size from a pin's head to the size of a lentil, and of a black-brown colour. A piece of the stomach was embedded in paraffin and stained. Examined under the microscope, it was found that the ulcers did not penetrate into the submucosa, but that only the mucous membrane was ulcerated. It was a remarkable fact that blood or blood-pigment could not be detected microscopically at the transverse sections.

It may be assumed that these ulcers were connected with the sudden death of the animal, but it is doubtful whether there exists any connection between the injection of the acetyl compound of methyl ester of anthranilic acid, and the presence of the ulcers in the stomach.

Experiment No. 10. A small dog weighing about 5 kilograms received a subcutaneous injection of 1 cc of the pure undiluted substance. The animal remained healthy.

Experiments No. 11 and 12. The same dog remained in good health after being injected with 1.2 g of the substance in dilution, and 1.8 cc of the undiluted substance.

All the specimens of urine formed with Florence-solution a brown precipitate, which, however, did not crystallise out. After adding soda liquor and an excess of hydrochloric acid, the characteristic needles were never precipitated, neither immediately, nor subsequently.

The urine of the guinea pig, which possessed an aromatic odour, was repeatedly treated with Florence-solution, and each time extracted with ether in which the precipitate dissolved. After driving off the ether, the residue was heated on a water bath until iodine was no longer sublimed, and it was then absorbed with a small quantity of water. After one week a few druses had crystallised out, which with potassium ferricyanide and ferric chloride formed a blue precipitate. They resembled the crystals mentioned on page 123.

The urine of the two rabbits had a strong characteristic odour and was free from albumin, but after adding soda liquor it possessed a very powerful reducing-action on copper sulphate, even when the temperature was but slightly raised. At first bright-yellow protoxide hydrate was formed, then red protoxide of copper. Salts of silver and of gold were also reduced.

As the presence of sugar was suspected, a portion of the urine of the rabbit which had received 0.55 g of the acetyl compound of methyl ester of methyl anthranilic acid (comp. experiment No. 9), was fermented with yeast. The sugar test gave positive results, the quantity of sugar found being 0.6 per cent.

The remaining portion of the urine was treated in the same manner as that of the guinea pig. After one week small druses and verruciform and fascicular crystals were found on the bottom of the vessel.

The urine of the other rabbit was treated with sulphuric acid until it had a pronounced acid reaction; it was then evaporated to the consistency of syrup, again rendered alkaline, and extracted with ether. The ethereal extract showed a blue fluorescence. After adding a few cc water, the ether was driven off, and there were then floating on the water a few oil-drops of a yellowish colour. One of these was removed with a spatula, the spatula round

the oil-drop carefully cleaned, and then placed in a solution of potassium ferricyanide and ferric chloride. The solution assumed an intense blue colour. The other oil-drops, after treatment with Florence-solution, produced beautiful fascicular crystals.

The urine of the dogs contained neither albumin nor sugar. The ethereal extract of the urine which had first been acidified with sulphuric acid, and after concentrating had been rendered alkaline with soda liquor, also showed a blue fluorescence, but only slightly. After driving off the ether, only a few small oil-drops floated on the water which had been added, and these formed a strong blue precipitate with iron.

Experiment No. 13. A medium-sized rabbit received a subcutaneous injection of 1,0 g of a solution of methyl ester of acetyl methyl anthranilic acid from the second consignment. After half an hour the animal became sleepy, and extended the fore legs. When placed in the dorsal position it turned over with difficulty. Pulsation, respiration and reflex-action remained normal. After 4 hours the animal had to some extent recovered.

The urine secreted in 48 hours had an alkaline reaction, contained no albumin, reduced copper solution, and gave a positive phenylglucosazone-test. By means of the fermentation-test it was found to contain 1,1 per cent. sugar. The urine was now acidified with sulphuric acid, slowly evaporated almost to dryness, again rendered alkaline with soda, and extracted with alcohol. After driving off the alcohol, the residue was extracted with ether. The latter showed an intense blue fluorescence. When the ether, after adding a small quantity of water, had again been driven off, there floated on the water numerous small and most minute drops of oil which showed all the reactions of methyl ester of methyl anthranilic acid.

Experiment No. 14. A medium-sized dog received a subcutaneous injection of 3,0 g of a solution of the substance received with the second consignment. This dose did not give rise to any symptoms. The urine of 48 hours measured only 30 cc. It had an alkaline reaction, and contained neither albumin nor sugar. The urine was treated in the same manner as in the last experiment. Fluorescence of the ether could not be observed with certainty. After driving off the ether, no oil-drops floated on the added water. Although this liquid produced an intense blue precipitate with potassium ferricyanide and ferric chloride, the reduction of metal salts was only slight.

Finally, the urine of the frogs which had received an injection of the acetyl compound, formed with Florence-solution a precipitate, from which, however, no crystalline needles were precipitated when soda and hydrochloric acid were added, a proof that the acetyl compound was not present in the urine.

As the presence of methyl ester of methyl anthranilic acid was suspected, the small residue of an ethereal extract of the carefully evaporated urine was treated with potassium ferricyanide and ferric chloride. A strong blue precipitate confirmed the supposition.

As is shown by the experiments on warm-blooded animals, the acetyl compound of methyl ester of methyl anthranilic acid appears to be fairly indifferent for the organism of the dog, as doses of even 3,0 g were tolerated by a medium-sized animal without the slightest demonstrable injuries to the organs, and without general disturbances. Nor was the appetite reduced. No sugar was excreted by the organism.

With the guinea pig and the rabbit the conditions are different. After the introduction of moderate doses, the substance causes in these animals at first slight disturbances of the co-ordination, but soon afterwards they become stupefied. The narcotic effect is, however, not prolonged. After stronger doses the central nervous system becomes paralysed. For guinea pigs the fatal dose is 1.0 g per kilogram weight. Apart from these nervous symptoms, the substance produces in the rabbit a considerable excretion of sugar, which can be readily detected by the fermentation- and phenylglucosazone-tests.

The acetyl compound of methyl ester of methyl anthranilic acid is not stable in the organism of frogs, guinea pigs, rabbits and dogs, but is excreted as methyl ester of methyl anthranilic acid after the acetyl-group has been split off.

On micro-organisms the acetyl compound of methyl ester of methyl anthranilic acid has no influence. The development of *Bacterium coli*, *Staphylococcus albus*, and *Bacillus subtilis* — the cultures had been inoculated into about 4 cc peptone-water — was in no way impaired by the addition of 1 cc of a 3 per cent. solution acting for 3 days.

The question now presented itself, whether per contra the bacteria had exerted any action on the substance. Such action, in view of the composition of the substance, and of the results of the experiments on animals, could, naturally, only have consisted of the splitting off of the acetyl group.

When the bacteria had been in contact for 4 days with the acetyl compound of methyl ester of methyl anthranilic acid, the cultures were submitted to the following examination.

Culture of *Bacterium coli*.

1. To one part peptone-water were added, after acidification with one drop dilute sulphuric acid, a few drops of a solution of potassium permanganate. Although it was at once discoloured, the various hues observed with the solution of the pure sulphate of methyl ester of methyl anthranilic acid did not occur. Nor could a dirty-blue fluorescence of the peptone-water be recognised.

2. A small quantity of Florence-solution was added to one part peptone-water. Although a stronger precipitate was formed, no crystallisation took place even after several week's standing.

3. Another part was slowly evaporated, extracted with ether, and the ether driven off. The residue, treated with potassium ferricyanide and ferric chloride, formed only a very slight blue precipitate.

As a check, about 4 cc peptone-water which had also been charged with *Bacterium coli*, but to which no acetyl compound had been added, was evaporated to dryness and extracted with ether. The residue in this case also formed only a slight blue precipitate.

Culture of *Staphylococcus albus*.

The examination was conducted in the same manner as with *Bacterium coli*, and led to the same results.

Culture of *Bacillus subtilis*.

1. A portion of the peptone-water, after acidification, discoloured a solution of potassium permanganate. The change of colours was here also absent, but a dirty-blue fluorescence could be observed, which, however, was but very faint.

2. The precipitate formed after adding Florence-solution, did not crystallise out.

3. The residue from the ethereal extract of peptone-water, when treated with iron, formed a strong blue precipitate. But an equally strong precipitate was obtained from a pure peptone-water culture of *Bacillus subtilis*.

It follows that *Bacterium coli* and *Staphylococcus albus* have no influence on the acetyl compound of methyl ester of methyl anthranilic acid. Such a result was to be expected in the case of these two micro-organisms, for if the acetyl-group had split off from only one-twelfth part of the substance, the micro-organisms would have been destroyed. The slight blue reaction at any rate does not yet prove the presence of free methyl ester of methyl anthranilic acid.

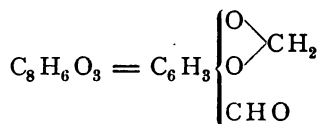
Bacillus subtilis, which is fairly indifferent towards free methyl ester of methyl anthranilic acid (compare page 124) appears, contrary to the other two micro-organisms, to split off a small part of the acetyl group. This conclusion at least would seem justified by the slight dirty-blue fluorescence of peptone-water after adding potassium permanganate.

Neither blood corpuscles nor hæmachrome undergo any change by the action of the acetyl compound of methyl ester of methyl anthranilic acid.

Piperonal.

Of the six possible dioxybenzaldehydes $C_6H_3(OH)_2 \cdot CHO$, of which three isomers have been obtained by means of chloroform-reaction from the three dioxybenzenes (pyrocatechol, resorcinol, and hydroquinone), $[H_2O + CHCl_3 + C_6H_4(OH)_2 = C_6H_3(OH)_2 \cdot CHO + 3 HCl]$ protocatechuic aldehyde is worthy of notice, as it is the substance from which piperonal and vanillin are derived — two bodies which have recently acquired great importance.

Piperonal, also called heliotropin:



is methylene ether of protocatechuic aldehyde. It is found regularly in oil of spiræa, i. e. the oil of *Spiræa Ulmaria*, and in many kinds of vanilla.

Piperonal is produced on a large scale by treating piperic acid, or — and now almost exclusively — safrol and isosafrol with oxidising agents. It forms inch-long lustrous crystals (from water), is soluble in 500 to 600 parts cold water, readily in alcohol, in every proportion in ether and hot alcohol. The melting point lies at 37°, the boiling point at 263°. It behaves generally as benzaldehyde. It is a remarkable fact that it does not give the characteristic reduction of salts of copper, gold, etc. by aldehydes. On oxidation it forms the corresponding piperonylic acid.

Piperonal plays an important part in the perfumery industry. It possesses a penetrating, coumarin-like odour, which strongly reminds of the actual perfume of the heliotrope flower. It is used in the manufacture of extraits, sachets, and soaps. When exposed to the sun, the crystals acquire a yellowish-brown colour, and lose the perfume completely.

According to the experiments made by Dr. Ricardo Frignani (comp. New York Medical Record), heliotropin possesses antipyretic and antiseptic properties. The antipyretic action is not very energetic, but in many cases sufficient. It is best administered in doses of 15 grains 3 to 4 times daily, but larger doses are also tolerated quite well. Its antiseptic action is stronger, and as it is harmless even in doses of 1/2 to 1 drachm, it deserves a high place among similar remedies.

According to O. Wimmer, "Further experimental examinations respecting piperonal. Thesis (Liebreich) Berlin", piperonal checks the action of pepsin and pancreas, the fermentation of lactic acid, putrescence, but not the action of yeast. It reduces the temperature of animals in a normal or feverish condition (also clinical observation).

More detailed examinations of the behaviour of piperonal in the animal body have been made by Dr. A. Heffter. In the organism of the rabbit (4.0 g were injected), piperonal was converted into the allied piperonylic acid, which could be precipitated from the alcoholic extract of the urine by means of hydrochloric acid. It was remarkable that here no combination had taken place with glycocholic acid, as this is the case with all aromatic monocarboxylic acids, if they contain not more than one hydroxyl-group.